PB81-144453

Preventing Haloform Formation in Drinking Water

South Dakota School of Mines and Technology
Rapid City

Prepared for

Municipal Environmental Research Lab.
Cincinnati, OH

Aug 80

U.S. Department of Commerce
National Technical Information Service
NTIS.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/2-80-091		PB81 144453

4. TITLE AND SUBTITLE	5. REPORT DATE
PREVENTING HALOFORM FORMATION IN DRINKING WATER	August 1980 (Issuing Date)
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Leland L. Harms and Robert W. Looyenga	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
South Dakota School of Mines and Technology Rapid City, South Dakota 57701	1CC824
	11. CONTRACT/GRANT NO.
	R805149-01-0
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Municipal Environmental Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268	Final 5/77 - 2/79
	14. SPONSORING AGENCY CODE
	EPA/600/14

15. SUPPLEMENTARY NOTES

Project Officer: O. Thomas Love, Jr. (513) 684-7281

16. ABSTRACT

The Huron, South Dakota, water distribution system was monitored for trihalomethanes at several locations. Deposits from within the distribution system were evaluated as potential precursor material and were found to be precursors for the haloform reaction. Field tests designed to determine the extent of trihalomethane formation that occurs as a result of the pipe deposits were inconclusive. The deposits appear to be a precursor source, but they do not substantially alter the terminal trihalomethane concentration.

Ammonium sulfate was used to convert to a combined chlorine residual in the distribution system. A significant drop in trihalomethane concentrations was obtained along with maintenance of adequate disinfection. Primary disinfection was obtained by lime softening followed by a free chlorine residual.

Land used upstream from the raw water intake was evaluated for potential chloroform formation. Peak concentrations occurred near marshes, where cattle watered, and where the river was stagnant.

Nine raw water quality parameters were monitored and correlated with THM formation. The best correlations were obtained with specific conductance and turbidity.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Chlorine-containing compounds Chlorination Disinfection, disinfectants Chloroform	Water treatment Potable water Agricultural wastes	13B

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
	UNCLASSIFIED	101
RELEASE TO PUBLIC	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE

☆ U.S. GOVERNMENT PRINTING OFFICE:1980--657-165/0102

United States
Environmental Protection
Agency

Municipal Environmental Research
Laboratory
Cincinnati OH 45268

EPA-600/2-80-091
August 1980

PB81-144453

Research and Development

EPA

Preventing Haloform Formation in Drinking Water

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

EPA-600/2-80-091
August 1980

PREVENTING HALOFORM FORMATION IN DRINKING WATER

by

Leland L. Harms
Robert W. Looyenga
South Dakota School of Mines and Technology
Rapid City, South Dakota 57701

Grant No. R805149-01-0

Project Officer

O. Thomas Love, Jr.
Drinking Water Research Division
Municipal Environmental Research Laboratory
Cincinnati, Ohio 45268

This study was conducted
in cooperation with
South Dakota School of Mines and Technology
Rapid City, South Dakota 57701

MUNICIPAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

DISCLAIMER

This report has been reviewed by the Municipal Environmental Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

Halogenated organics are produced during the chlorination step in water treatment. The results of research to minimize the production of these contaminants by modifying disinfection practices are examined in this publication.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

ABSTRACT

Previous work at Huron, South Dakota had achieved a reduction in haloforms in the drinking water delivered to the consumers. However, the concentrations of both chloroform and bromodichloromethane were still considered to be excessive, primarily due to the growth of these compounds within the distribution system.

The water distribution system was monitored for trihalomethanes at several locations. Deposits from within the distribution system were evaluated as potential precursor material and were found to be precursors for the haloform reaction. Field tests designed to determine the extent of trihalomethane formation which occurs as a result of the pipe deposits were inconclusive. It appears that the deposits are a precursor source, but they do not substantially alter the terminal trihalomethane concentration.

Ammonium sulfate was used to convert to a combined chlorine residual in the distribution system. A significant drop in trihalomethane concentrations was obtained while still maintaining adequate disinfection. Primary disinfection was obtained by lime softening followed by a free chlorine residual.

Land used upstream from the raw water intake was evaluated for potential chloroform formation. Peak concentrations occurred near marshes, where cattle watered, and where the river was stagnant.

Nine raw water quality parameters were monitored and correlated with THM formation. The best correlations were obtained with specific conductance and turbidity.

This report was submitted in fulfillment of Grant No. R805149-01 by the South Dakota School of Mines and Technology under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period of from May 23, 1977 to June 20, 1978 and work was completed as of February 28, 1979.

CONTENTS

Foreword iii
Abstract iv
Figures. vii
Tables viii
List of Abbreviations and Symbols. ix
Acknowledgments. x

1. Introduction 1
   General 1
   Scope of Work. 1
2. Conclusions 3
3. Recommendations 4
4. Previous Research at Huron. 5
   Introduction 5
   Results 5
   Recommendations. 5
5. Water Treatment at Huron. 7
   History. 7
   James River Water Quality. 8
   Treatment Process of the 1949 Plant. 9
   Treatment Process of the 1978 Plant. 11
6. Experimental Methods. 15
   General. 15
   Field. 15
      Sampling Stations 15
      Sampling Location 16
      Sample Handling 16
      Field Tests 18
   Laboratory 18
      Reagents. 18
      Analytical Procedures 18
7. Results 24
   Distribution System. 24
   Raw Water Parameters 28
      Temperature 29
      Specific Conductance. 29
      Turbidity 29
      Land Use. 36
      Seasonal Variations 36
   Monitoring Trihalomethanes 39
   Disinfection with pH 39

CONTENTS (Continued)

Previous Experience Using Combined Chlorine 45
Kinetics of Chloramine Formation 48
Simulation of Disinfection with Chloramines 49
Start-up Using Combined Chlorine. 51
Full-Scale Operation with Combined Chlorine 52
Operation with Combined Chlorine. 56
Economics 58

References 60
Appendices

A. Full Plant and Distribution System Data 62
B. Residence Time in the Distribution System 71
C. Pipe Material Test. 72
D. In Pipe Test 74
E. Raw Water Quality Data 77
F. PTHM Vs. Chlorine Dose 79
G. Chlorine Dose at the Treatment Plant 81
H. River Trip Data 82
I. Total Organic Carbon Data 84
J. Total Coliform Data 85
K. Artificial Spiking Data 88

FIGURES

Number		Page
1	Process Flow Diagram for Water Treatment at Huron Prior to December 1977	10
2	Process Flow Diagram for Water Treatment at Huron After December 1977	12
3	Sampling Station in the Distribution System	17
4	Graphical Representation of Four Trihalomethane Parameters	20
5	Potential Chloroform Concentration From Pipe Material at a Chlorine Dose of 3.43 mg/l	25
6	Potential Chloroform Concentration From Pipe Material at a Chlorine Dose of 18.2 mg/l	27
7	PTHM vs. Chlorine Dose (5/10/78)	30
8	Effect of Raw Water Temperature on Chloroform Concentration	31
9	Effect of Temperature on $CHCl_3$ Formation at pH 11	32
10	Specific Conductance as an Indicator of Potential Chloroform Concentration	33
11	Effect of Time and pH on $CHCl_3$ Formation at 20°C	34
12	Turbidity as an Indicator of Chloroform Concentration	35
13	Potential Chloroform Formation Within the James River	37
14	Variation of Chloroform Concentration	38
15	Variation of Bromodichloromethane Concentration	40
16	Coliform Disinfection by pH	42
17	Comparison of Germicidal Efficiency of Hypochlorous acid, Hypochlorite Ion, and Monochloramine	46
18	THM Reduction Using Ammonium Sulfate	55

TABLES

Number		Page
1	James River Water Quality (4)	8
2	Typical Chemical Feed Rates at Water Plant Prior to December 1977	11
3	Chemical Feed Rate (Typical) at Water Plant After December 1977	14
4	Laboratory Tests and Procedures of Analysis	21
5	Total Organic Carbon Concentrations on February 14, 1978.	26
6	Optimum pH Ranges for Some Common Bacteria (16)	41
7	Reduction in Total Coliforms From Station 2N to Station 5N Due to Lime Softening	43
8	Incubation of 100 Cells/ml of Pathogens in Limed Water	44
9	Incubation of 1,000 Cells/ml of Pathogens in Limed Water.	44
10	Results of Chloramination Simulation	50
11	Comparison of Two Different Ratios of Chlorine to Ammonia-Nitrogen	52
12	THM Concentrations During Transition Period	54
13	THM Concentrations on June 27, 1978	57
14	Ammonia Concentrations Which Result in 0.2 mg/l Unionized Ammonia (NH_3)	57
15	Effect of Chlorine Vs. Chloramines on Total Plate Counts.	58
16	Estimated Costs of Disinfection Alternatives for a 5 MGD Plant	59

LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

EPA	--United States Environmental Protection Agency
NORS	--National Organics Reconnaissance Survey
THM	--Trihalomethane(s)
ppb	--Part per billion
eqn	--Equation
Inst THM	--Instantaneous Trihalomethane Concentration
Term THM	--Terminal Trihalomethane Concentration
THMFP	--Trihalomethane Formation Potential
TTHM	--Total Trihalomethane Concentration
PTHM	--Potential Trihalomethane
cfs	--Cubic feet per second
BDCM	--Bromodichloromethane
$CHCl_3$	--Chloroform
ND	--Not Detectable

ACKNOWLEDGMENTS

The cooperation of the municipal officials and employees at Huron, South Dakota is gratefully acknowledged. Special appreciation is extended to Mr. Glenn Housiaux, City Engineer; Mr. Harold Root, Water Treatment Plant Superintendent; and the operating staff of the Huron Water Treatment Plant.

The research was truly a team effort. Messrs. Tom Norman, Dan Hoyer, and P. A. Sachdev were deeply involved in both field and laboratory work. Mr. Larry Doss was the field engineer on site in Huron. Bacteriological testing dealing with pathogens was conducted in the laboratories at South Dakota State University, and supervised by Dr. Paul Middaugh.

Technical assistance and support were given throughout the project by Mr. A. A. Stevens and Dr. O. T. Love of EPA's Municipal Environmental Research Laboratory.

SECTION 1

INTRODUCTION

General

A drinking water quality survey conducted by EPA identified high levels of certain organic compounds in the drinking water at Huron, SD (1). In order to provide technical assistance to the City of Huron to aid in correcting the problem, a federal grant allowed an on-site investigation which led to some treatment modifications (2). The formation of chloroform was substantially reduced during the water treatment process.

Although the initial work at Huron did improve the water quality, it was felt that additional work could result in still lower trihalomethane levels in the water. Also, the study raised some questions regarding the formation of organic compounds within the distribution system and sources of precursors. Consequently, an additional project was begun at Huron and the results of this work are reported in this document. The specific objectives of the new project were:

(1) Study the use of chloramines as a disinfectant and, if suitable, adapt this disinfection procedure to the full-scale water treatment process at Huron to obtain total haloform reduction.

(2) Monitor the distribution system to detect aftergrowth of haloforms in the system, and determine if this aftergrowth is a result of precursors present in the distribution system.

(3) Attempt to reduce the potential for chlorinated hydrocarbon formation by identifying the primary source(s) and recommending steps to reduce the precursors. Sources to be considered are agricultural runoff, point sources, and biological growths in stagnant water.

(4) Substantially reduce the bromodichloromethane formed in the water treatment process.

Scope of Work

All field work was conducted in or near the city of Huron, South Dakota. Samples were collected from the water treatment plant and the distribution system which serves the citizens of Huron. Samples were not collected from pilot plant facilities or other microscale operations.

Background data on the water treatment processes, the raw water quality, and haloforms in the distribution system were collected during the summer and early fall of 1977. During this time, the water treatment plant at Huron was undergoing expansion and modification. Start-up of the altered treatment began in December of 1977 with several start-up problems, as would be expected. Initial experimentation with the use of chloramines as a disinfectant (the ammonia being supplied from ammonium sulfate) resulted in the full-scale application of this process in early May of 1978. Extensive monitoring was conducted until early June. Raw water quality and haloforms within the distribution system were also monitored during this period.

The majority of the analytical work was performed on the campus at the South Dakota School of Mines and Technology. Periodically some testing was done in the laboratory at the Huron Water Works. Total plate counts and some pathogenic work was done through a cooperative agreement with South Dakota State University.

SECTION 2

CONCLUSIONS

1. Disinfection is effectively achieved by the lime softening process in which the pH is raised above eleven.

2. Maintaining a disinfection residual with combined chlorine is an effective means of reducing the concentrations of both $CHCl_3$ and BDCM.

3. Disinfection with combined chlorine eliminated taste and odor problems at Huron.

4. The proper application of combined chlorine can be the most economical means of reducing THM concentrations.

5. Ammonium sulfate is a convenient and effective source of ammonia for chloramine production.

6. The increase in THM concentrations in the Huron distribution system closely follows residence time.

7. Deposited material within the pipelines of the Huron distribution system contains organic precursors; however, their contribution to THM formation appears minimal.

8. Nonprecursor organic material competes favorably for available free chlorine under chlorine limited conditions. Such conditions lead to an inverse relationship between THM levels and chlorine demand, and result in the THM formation being dependent upon the chlorine dose.

9. For the Huron raw water, THMFP is directly related to turbidity and specific conductance.

10. Growth curves indicate a critical pH above which chloroform forms much more readily and to a greater extent.

11. Agricultural runoff appears to be a significant source of precursors for the haloform reaction, but it does not appear to be a significant source of bromide.

12. The potential for chloroform formation in the Huron raw water is highest in areas of marsh growth, where cattle water and where the water is very stagnant.

SECTION 3

RECOMMENDATIONS

1. Total plate counts of the Huron water should be monitored periodically to assure that no long term degredation of the drinking water occurs.

2. The type(s) of organic precursors present in agricultural runoff should be determined in order to aid in planning better land management and pollution control.

3. A study of the sources of bromide should be made in order to better control the concentrations of brominated compounds which are potentially of greater concern than chloroform.

4. A simple qualitative-semiquantitative field test should be developed for the trihalomethanes.

SECTION 4

PREVIOUS RESEARCH AT HURON

Introduction

Results of the NORS (1) sampling by EPA indicated high chloroform and bromodichloromethane levels in the drinking water at Huron, South Dakota. Initial work was begun to more precisely define the problem and to suggest ways of obtaining lower haloform concentrations. This earlier work is reported in a document available from EPA (2). The results and recommendations are repeated as they were the basis for the additional experimentation reported in this document.

Results

Samples were collected routinely from seven sampling locations within the water treatment facility and monitored for the THM. Some additional samples were taken from the distribution system. The treatment facility used lime for softening. Changing the location of the prechlorine dose resulted in a substantial reduction in haloform concentrations in the product water. Briefly, the work showed that:

(1) Haloforms form in high concentrations at the point of chlorination and lime addition.

(2) A 75% reduction in chloroform in the finished effluent was obtained by changing the point of chlorination from before the flocculation basins to the recarbonation basin.

(3) Chloroform formation is proportional to pH. However, trying to lower the pH for chloroform reduction resulted in water instability if decreased below a pH of nine.

(4) THM concentrations increase after entering the distribution system.

(5) Bromodichloromethane formation is not as pH dependent as chloroform.

Recommendations

Recommendations which evolved from the study were:

(1) The disinfection should continue at the revised location.

(2) Additional data on bromodichloromethane formation should be gathered. This constituent was not significantly reduced.

(3) Additional work should be done on the aftergrowth of haloforms within the distribution system.

(4) Identification of the precursor source(s) should be considered in an attempt to reduce the potential for chlorinated hydrocarbon formation. Possibilities to be evaluated should include:

    a. point sources upstream

    b. the local practice of disposing of dead animals in the stream

    c. precursor increase from biological growth in stagnant water

    d. agricultural runoff as a precursor source

(5) Alternate methods of disinfection should be considered such as the use of ozone, chloramines and chlorine dioxide.

SECTION 5

WATER TREATMENT AT HURON

History

Huron, South Dakota is located in the east central quarter of South Dakota. The surrounding terrain is relatively flat. In some places the James River is above the surrounding area. Therefore, during high flows, the area adjacent to the James River is flooded, and recedes through infiltration, or flows to a drainage basin which runs into the James. This river is a slow meandering river with depths ranging from one foot to twenty feet, and alternates between narrow to very wide in the fifteen miles from the James Diversion Dam to the raw water intake at Huron. A 27 year history of the James River reveals that there is zero flow about 40 percent of the time, that 75 percent of the time the flow is less than 30 cfs, and that the mean annual flow is 259 cfs (3).

The first public water supply for the town of Huron was the James River. In 1883, water was pumped directly from the James River into the distribution system without any treatment. In 1886, artesian water was discovered in the Dakota Sandstone at depths of nine hundred feet to eleven hundred feet. The city discontinued use of the James at this time and developed four wells which produced highly mineralized artesian water. In 1914, the city switched back to James River water because the artesian supply became inadequate to meet the demand (4). A 1.5 MGD treatment plant to clarify and purify the water was constructed at this time. The capacity was expanded to 3 MGD in 1928.

The drought in the 1930's caused the river water supply to fall short of the demand. Wells were drilled again in the Huron vicinity, but this water was also highly mineralized. The wells were put in use in 1934, and the water was distributed with chlorination being the only water treatment. These wells, in conjunction with the river supply, were used only sparingly until 1951, when the wells were again used for a short period of time.

In 1948 and 1949, a new 4.15 MGD water treatment plant was constructed to treat water for purification, clarification, and softening. The level of the Third Street Diversion Dam was also raised to facilitate more water storage (4).

In 1959 and 1960, there was a shortage of James River water, forcing Huron to start the well fields again to fulfill the water demand. The total municipal water supply for Huron has been obtained from the James River since 1961.

In 1964, the Bureau of Reclamation constructed the James Diversion Dam, located about fifteen miles north of Huron. This dam replaced the old Spink County Reservoir, providing additional storage for Huron's water supply. Since the completion of this dam, the well fields have been abandoned and pumping and other equipment disconnected (4).

The most recent modification to the water treatment plant was finished in December of 1977. Extensive revisions were made which increased the plant capacity to 7.4 MGD.

James River Water Quality

The water quality is extremely variable as shown in Table 1. Agricultural runoff, upstream wastewater discharges, dead animals disposed in the stream, and seasonal variations all combine to make the raw water difficult to treat for domestic use. According to the operator's log at the treatment plant, the river water pH usually falls within a range of from 7.5 to 8.5.

TABLE 1. JAMES RIVER WATER QUALITY (4)

Constituent	Raw Water		
	Low	High	Average
Total solids, ppm	271	2180	547
Total hardness, ppm	131	963	256
Iron, ppm	0.02	0.05	-
Calcium, ppm	53	158	-
Chloride, ppm	51	157	-
Sulphates, ppm	100	785	167
Bicarbonates, ppm	98	812	248
Fluorides, ppm	0.3	0.4	-
Nitrates, ppm NO_3	0.3	2.0	-
Magnesium, ppm	33	119	-
Sodium, ppm	29	352	80
Potassium, ppm	14	25	-

Treatment Process of the 1949 Plant

In the old treatment plant at Huron, water treatment consisted of chemical addition, sedimentation, flocculation, clarification, recarbonation, filtration and chlorination. A schematic drawing of the old plant is shown in Figure 1 and a process description follows:

Process	Description
River to plant	Raw water is pumped from the James River at an intake located about one hundred feet upstream from the Third Street Diversion Dam.
Initial chemical addition	Potassium permanganate, activated carbon, alum, and a polyelectrolyte (Nalco 607) are dispersed in the water.
Presedimentation	Settling of one hour duration at a flow of 6 MGD.
Rapid mix	Dispersion of lime, soda ash (occasionally) and sodium aluminate (Nalco 617) in a rapid mix basin.
Flocculation	Gentle stirring of the water-chemical mixture. Detention time at 6 MGD is about 1.5 hours.
Clarification	Settling of solids with a detention time of 2 hours at 6 MGD.
Recarbonation	Adjustment of pH with carbon dioxide to obtain stable water. Fluoride, and polyphosphate (Nalco 918) are added at this basin.
Prechlorination	Initial dose of chlorine for longer filter runs.
Gravity filters	Anthrafilt filtering media used for filtration.
Postchlorination	A final chlorine dose for disinfection in clear well and distribution system.
Clear well storage	Temporary storage of the finished water before entering the distribution system and high level storage.

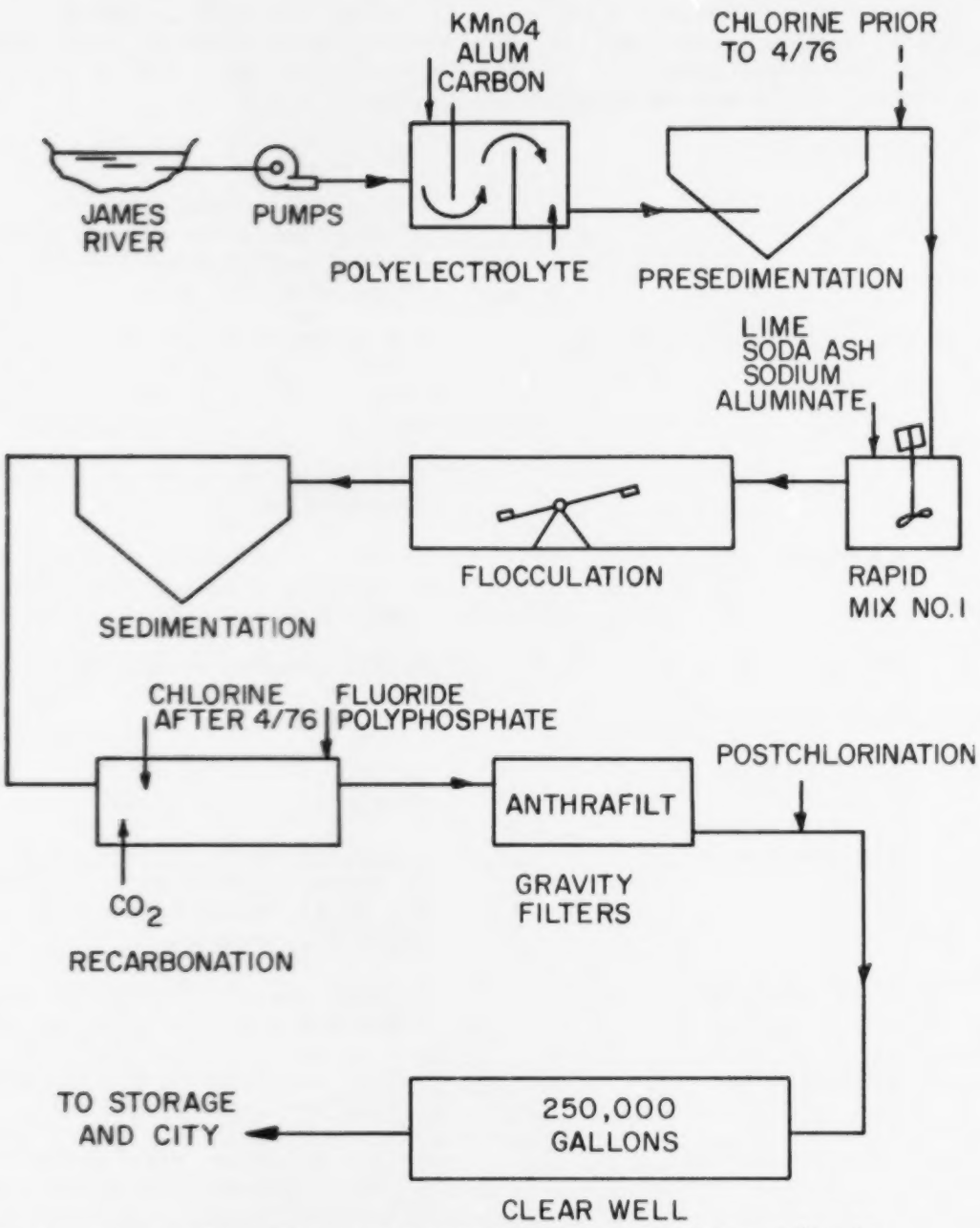

Figure 1. Process flow diagram for water treatment at Huron prior to December 1977.

Some typical feed rates for the aforementioned chemicals in the old plant are given in Table 2. These feed rates vary from day to day. The feed rates depend on the quality of the raw water and the plant operation.

TABLE 2. TYPICAL CHEMICAL FEED RATES AT WATER PLANT PRIOR TO DECEMBER 1977*

CHEMICAL	FEED RATE (ppm) 9/8/75	5/24/76
Powdered Activated Carbon	2.2	28.0
Potassium Permanganate	0.98	9.37
Alum	29.0	22.0
Polyelectrolyte (Nalco 607)	0.80	0.98
Prechlorine Dose	6.8	4.0
Lime	152.0	135.0
Sodium Aluminate (Nalco 617)	9.6	6.2
Soda Ash	0	0
Carbon Dioxide	36.0	47.0
Fluoride	1.2	1.2
Polyphosphate (Nalco 918)	2.0	1.75
Postchlorine Dose	2.6	4.0

*Operator's Log, Huron Water Works

Treatment Process of the 1978 Plant

Along with the increase in capacity which was attained by various modifications, some changes in the unit processes were also made. The major changes were the addition of more presedimentation units; and the combining of the mixing, flocculation, and sedimentation functions into two solids upflow basins. Other changes included converting the existing flocculation tanks to recarbonation and chlorine contact units, new chlorination and chemical handling equipment, and additional chemical storage area. A schematic drawing of the new plant is shown as Figure 2. A process description is as follows:

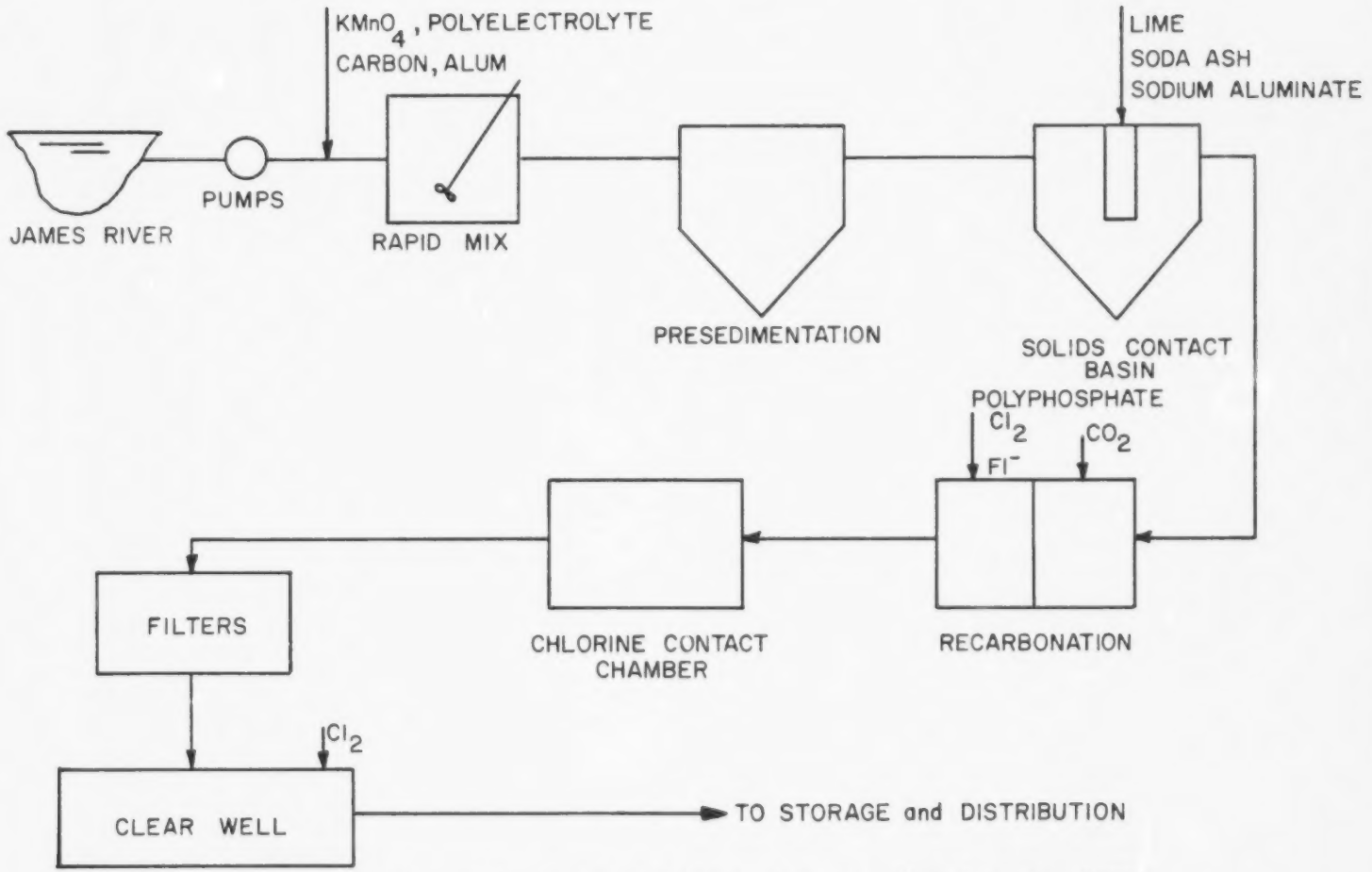

Figure 2. Process flow diagram for water treatment at Huron after December 1977.

Process	Description
River to plant	Raw water is pumped from the James River at an intake located about one hundred feet upstream from the Third Street Diversion Dam.
Initial chemical addition	Potassium permanganate, activated carbon, alum, and a polyelectrolyte (Nalco 607) are dispersed by mixing.
Presedimentation	Settling of from one hour to almost four hours duration.
Chemical addition	Lime, soda ash (occasionally) and sodium aluminate (Nalco 617) are added to the center of the upflow basin.
Upflow basin	Solids are settled further and filtered through a sludge blanket approximately six feet above the floor of the tank. Detention time in this tank is approximately 0.76 hours at 6 MGD.
Recarbonation basin	Adjustment of pH with carbon dioxide to obtain stable water. Fluoride, polyphosphate (Nalco 918) are added at this basin.
Prechlorine	Initial chlorine dose to lengthen filter runs.
Chlorine contact tank	Provides time for the chlorine to come in contact with the water before filtration. Detention time is about 0.66 hours at 6 MGD.
Gravity filters	Anthrafilt filtering media used for filtration.
Post chlorination	A final chlorine dose for disinfection in the clear well and distribution system.
Clear well	Temporary storage of finished water before entering the distribution system and high level storage.

The flow diagram shown in Figure 2 was followed after December 1977 except for the following instances:

(1) During initial start-up, until February 17, 1978, the recarbonation and chlorine contact basins were by-passed and the water flowed directly to the filters.

(2) Sometime near the beginning of April, the carbon dioxide was inadvertantly applied just prior to filtration, after the pre-chlorine dose. This resulted in high THM concentrations, and the recarbonation was corrected on April 30, 1978.

(3) Intentional modification of the disinfection process was made by the addition of ammonium sulfate in May of 1978. This is described completely in a subsequent section.

Typical chemical feed rates for the new plant are given in Table 3.

TABLE 3. CHEMICAL FEED RATE (TYPICAL) AT WATER PLANT AFTER DECEMBER 1977

CHEMICAL	FEED RATE (mg/l) 2/28/78
Powdered Activated Carbon	15
Potassium Permanganate	3.28
Alum	35*
Polyelectrolyte (Nalco 607)	1.93
Lime	473
Sodium Aluminate	6.21
Soda Ash	76.2
Carbon Dioxide	40.4
Prechlorine Dose	4.62
Fluoride	1.2
Polyphosphate (Nalco 918)	unknown dose
Postchlorine Dose	9.56

*No alum is added unless turbidity exceeds 2 Jackson Candle Units. This is an approximate dosage.

SECTION 6

EXPERIMENTAL METHODS

General

Sample collection and analysis began on May 2, 1977 and continued through May 10, 1978. This time frame included stagnant summer conditions in the James River, fall and spring runoff, and stagnant conditions during the winter months. Therefore, the data presented in this report reflects the seasonal changes in the James River water quality.

The laboratory tests performed in this study may be grouped into three areas, i.e., (1) chemical-physical parameters of water quality, (2) trihalomethanes concentrations, and (3) biological activity. Chemical-Physical parameters which were routinely monitored are indicated in Table 4. Trihalomethanes (THMs) monitored consisted mainly of chloroform and bromodichloromethane. Due to their low concentrations, other THMs were of minor concern and were not generally determined.

The following laboratories were used for the testing of the Huron water samples. Field tests were conducted by the field engineer, at the water treatment plant at Huron, South Dakota. The THM determinations were performed in the Instrumental Analysis Laboratory in the Chemistry Building at SDSM&T. Three sets of total organic carbon samples were analyzed by EPA at the Municipal Environmental Research Laboratory, Cincinatti, Ohio and one set was analyzed by Dr. Robert Hoehn's laboratory at Virginia Polytechnic Institute and State University. Total plate counts and all work using *Salmonella* organisms were performed by Dr. Paul Middaugh at South Dakota State University. The remainder of the chemical-physical and biological tests were conducted in the Sanitary Engineering Laboratory in the Civil-Mechanical Engineering Building on the SDSM&T campus.

Field

Sampling stations. Sampling stations were carefully selected throughout the Huron treatment plant and distribution system in order to follow the progress of the treatment process and the effect of detention time in the distribution system. The location of the sampling sites within the treatment plant are indicated in Figures 1 and 2, and are as follows:

Station No.	Description
Station 1	- Raw water intake to treatment plant

Station No.	Description
Station 2	- Effluent from presedimentation tank
Station 3	- Effluent from rapid mixer
Station 4	- Effluent from flocculation tank
Station 5	- Effluent from sedimentation tank
Station 5.5N	- Effluent from recarbonation basin
Station 6	- Above gravity filters
Station 6.5	- Effluent from gravity filters and before post-chlorination
Station 7	- Clear well

Six sampling sites within the distribution system (see Fig. 3) were selected such that the residence time varied from a few hours to a few days. The samples collected from these sites were used to measure the increase in THM concentration in the distribution system and to monitor the disinfection effectiveness of combined chlorine. The following sampling sites were selected; they are listed in approximate order from shortest to longest residence time.

Sampling Location	Description
a. Masonic Building	- centralized, short detention time
b. 9th Street Standard Gas Station/A&M Radio	- centralized, medium detention time
c. Drive-in Liquor-West Side	- long detention time
d. Country Kitchen-South Side	- long detention time
e. Airport-North Side	- extremely long detention time

Sample Handling. The THM samples were collected and sealed bubble free in 60 ml glass bottles, previously cleaned and heated at 450°C. Samples from the distribution system were dechlorinated with sodium thiosulfate at the time of collection and were stored in ice or in a refrigerator until analyzed. Sample collection and handling procedures for the THM determinations were in close agreement with those used in the NORS (1).

The raw water samples collected for the physical-chemical tests were analyzed within two days. No preservation other than refrigeration was required except for the ammonia sample. This sample was preserved with

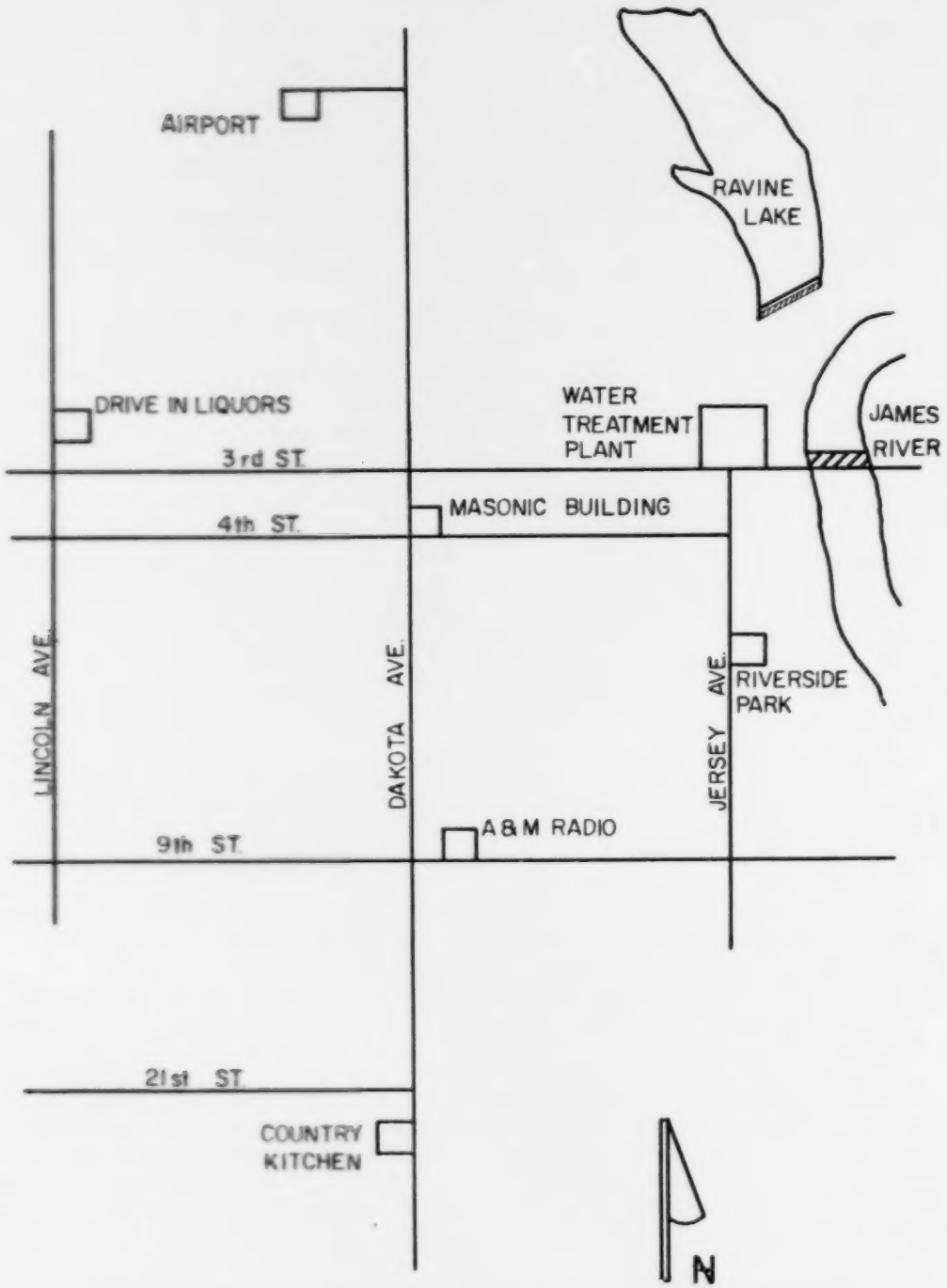

Figure 3. Sampling station in the distribution system.

0.8 mg/l concentrated sulfuric acid and was run the day following collection. All samples were stored in ice, shipped via bus, and then refrigerated at the laboratory.

Bacteria samples were collected in pre-sterilized "Whirl-pak" bags (Nasco product). Bacteria samples were always collected while the water treatment plant was operating. Samples with a high pH were neutralized with-1 N sulfuric acid; samples containing chlorine were dechlorinated with sodium thiosulfate. Bacteria samples were stored on ice and shipped by air freight. The coliform tests were always run within twenty-four hours and usually within sixteen hours after being collected in Huron.

Field Tests. Chlorine residual (free and total), temperature, and pH were determined in Huron by the field engineer. Chlorine was determined by a DPD field HACH kit and pH was determined by a pH meter. When it was necessary to artificially chlorinate or ammoniate in the field, standard solutions were shipped to the field engineer from the South Dakota School of Mines laboratory.

Laboratory

Reagents. All solutions and standards were prepared, when possible, from reagent grade chemicals. Chlorine demand free water was prepared according to "Standard Methods" (5). Chlorine water was prepared in the laboratory by diffusing chlorine gas in chlorine demand free water for approximately one minute. Measurements of the actual concentrations were made following appropriate dilutions with chlorine demand free water. Organic free water was prepared by purging distilled water at 20 ml/min for 11 minutes with helium.

Analytical Procedures. Bacterial determinations of total and fecal coliforms were performed by the membrane filter technique as described in "Standard Methods", Sections 909A and 909C respectively (5).

All THM determinations were performed by the purge and trap technique described by Bellar & Lichtenberg (6). A Varian Aerograph 705 Gas Chromatograph, equipped with a modified inlet system, a Tractor Model 310 Hall Electrolytic Conductivity Detector and a Varian A-25 Strip Chart Recorder were utilized in the determinations. Detailed instrumental parameters are reported in previous work (2).

Prior to analyzing samples on any given day, the trap was conditioned by placing it in the heated inlet port of the gas chromatograph and flushing with helium at 20 ml/min at 180°C for 4 minutes. Following conditioning of the trap a blank and two standards were generally run in order to calibrate the instrument. In addition a set of check samples provided by EPA was acceptably analyzed.

The analytical procedure used throughout the study was as follows:

1. Place the sample bottle in a water bath at 20°C and allow the temperature to equilibrate.

2. Using a 5 cc glass hypodermic syringe, transfer 5 ml of sample to the purging device.

3. Attach the trap to the exit port of the purging device and purge the sample for 11 min with helium gas at 20 ml/min.

4. Transfer the trap to the modified inlet port of the gas chromatograph and backflush (desorb) with helium at 20 ml/min at 180° C for 4 min.

5. Replace the trap with a plug, quickly raise the column temperature to 95° C and start the recorder.

6. Following 14 min at 95° C, program the column temperature at 8° C/min to 180° C.

7. Following 5 min at 180° C, reduce the column temperature to 30° C, or less, and proceed with the next sample.

As indicated in Table 4, the physical-chemical parameter tests were performed, for the most part, according to procedures in "Standard Methods" (5). The "In-Plant Chlorine Demand" is defined as the arithmetic difference between the total chlorine added and the chlorine residual measured at the time of sampling.

The last four tests listed on Table 4 were devoloped during the course of the project and are described in detail in the following paragraphs.

So that the reader may better understand the PTHM data, four definitions presented by Stevens and Symons (7) are given below (items one through four) along with a definition of PTHM, item 5. The four definitions used by Stevens and Symons are graphically represented in Figure 4. The PTHM concentration, as used in this report, would have a higher value than the Term THM concentration. The five definitions are:

(1) Instantaneous THM (Inst THM) concentration - the initial concentration of THM in water when sampled.

(2) Terminal THM (Term THM) concentration - the concentration of THM that occurs when the THM reaction is terminated, i.e. at the tap.

(3) THM formation potential (THMFP) - measured as the increase in THM concentration that occurs during the distribution system or storage period.

$$THMFP = \text{Term THM} - \text{Inst THM}. \qquad \text{EQN. 1}$$

(4) Total THM (TTHM) concentration - the summation of the concentrations of the individual trihalomethane species, reported in either mg/l or micromoles per liter.

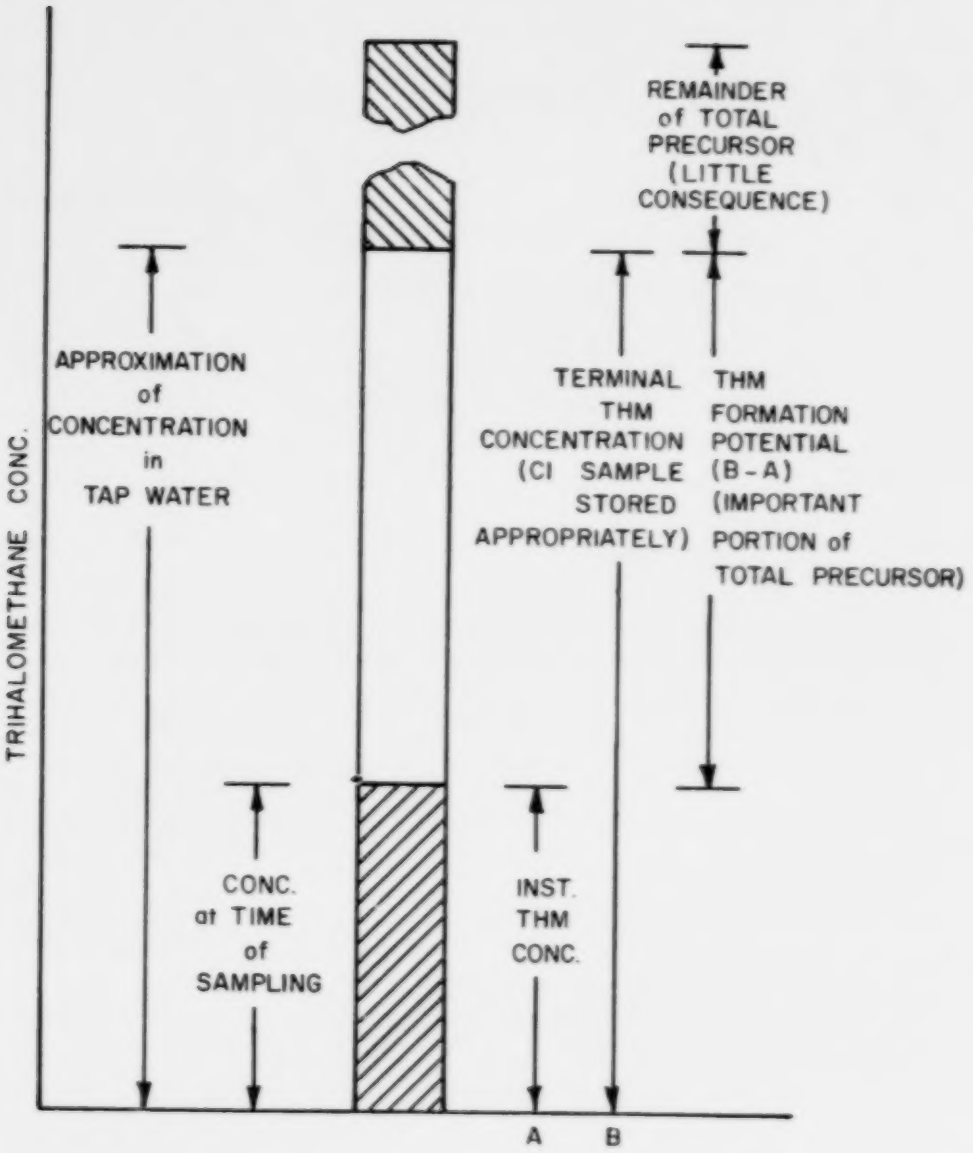
TRIHALOMETHANE CONC.
APPROXIMATION of CONCENTRATION in TAP WATER
CONC. at TIME of SAMPLING
INST. THM CONC.
TERMINAL THM CONCENTRATION (CI SAMPLE STORED APPROPRIATELY)
REMAINDER of TOTAL PRECURSOR (LITTLE CONSEQUENCE)
THM FORMATION POTENTIAL (B-A) (IMPORTANT PORTION of TOTAL PRECURSOR)
A
B

Figure 4. Graphical representation of four trihalomethane parameters, after Stevens and Symons (7).

TABLE 4. LABORATORY TESTS AND PROCEDURES OF ANALYSIS

Tests	Method of Analysis
pH	"Standard Methods" (5-460)
Temperature	"Standard Methods" (5-125)
Specific Conductance	"Standard Methods" (5- 71)
Ammonia	"Standard Methods" (5-381)
Chemical Oxygen Demand	"Standard Methods" (5-550)
Suspended Solids	"Standard Methods" (5- 94)
Volatile Suspended Solids	"Standard Methods" (5- 95)
Total Residue	"Standard Methods" (5- 91)
Turbidity	"Standard Methods" (5-132)
Chlorine Demand	"Standard Methods" (5-132)
In-Plant Chlorine Demand	See following text
Potential Trihalomethanes (PTHM)	See following text
Chlorine dose - THM Concentration Curve	See following text
Pipe Precursor Material Test	See following text
In Pipe Precursor Test	See following text

(5) Potential THM (PTHM) - the THM concentration obtained at optimum conditions of pH (pH=11), chlorine dose (20 mg/l), and retention time (3 days).

Potential Trihalomethane (PTHM, raw water)

1) Adjust a sample of raw water to pH 11 using NaOH.

2) Half fill two 300 ml BOD bottles with pH 11 raw water and dose for 20 and 25 mg/l chlorine respectively.

3) Readjust to pH 11 with NaOH, fill bottles with pH 11 raw water, stopper and mix.

4) Incubate in a 20°C refrigerator for seventy-two hours.

5) Collect and dechlorinate THM samples.

6) Measure free and total chlorine in the remaining solution.

7) Measure the THM concentrations.

The PTHM is defined as the THM concentration for a chlorine dose of 20 mg/l. This can be obtained from a straight line graph between the two chlorine doses and the concentration concurrent with 20 mg/l of chlorine. For centrifuged PTHM samples, the above procedure was used with the exception that after Step 1 the raw water is centrifuged for about one-half hour.

THM Concentration vs. Chlorine Dose (raw water).

1) Adjust the pH of a raw water sample to eleven with NaOH.

2) Half fill 300 ml BOD bottles with pH 11 raw water and add increasing dosages (from 0 mg/l to 40 mg/l) of free chlorine.

3) Readjust to pH 11 with NaOH, fill the bottles with pH 11 raw water, stopper and mix.

4) Incubate in a 20°C refrigerator for ninety-six hours.

5) Remove and dechlorinate THM samples.

6) Measure the free and total chlorine of the remaining solution.

7) Measure the THM concentrations.

8) Plot chlorine dose vs. THM concentration.

Pipe Material Test

1) Remove deposited material from section of pipe from distribution system.

2) Prepare a chlorine standard at pH 11.

3) Add varying amounts (e.g. 0 to 1 g) of pipe material to different 300 ml BOD bottles.

4) Fill the BOD bottles with the chlorinated water.

5) Incubate in a 20°C refrigerator for twenty-four hours.

6) Collect and dechlorinate THM samples.

7) Measure free and total chlorine on the remaining solutions.

8) Determine the THM concentrations for an indication of THM Precursors.

In Pipe Test

1) Flush a temporarily unused dead end main until the chlorine concentration approaches that of the clear well.

2) Immediately following flushing, collect a series of samples to establish baseline growth of THMs.

3) Periodically collect and dechlorinate THM samples from both the main and the baseline set. Assure that neither reaction is chlorine limited by measuring free and total chlorine in both pipe and baseline samples.

4) Measure and compare the THM concentrations of the pipe and baseline samples for indication of in-line precursor material.

SECTION 7

RESULTS

In meeting the objectives of the study, work was conducted in five major areas: (1) Problems associated with aftergrowth of THMs in the distribution system, (2) correlation of THM concentrations with raw water parameters, (3) correlation of THM concentrations with land use, (4) monitoring of THM concentrations, and (5) studies of the use of chloramine as a disinfection agent. Results of each of these areas of study follows.

Distribution System

The general problem of study regarding the distribution system was first identified in previous work at Huron (2). While modifications in the treatment process resulted in a reduction of the mean chloroform concentration from 222 to 59 ppb in the plant effluent, conditions within the distribution system resulted in a chloroform concentration at the consumers tap of about 127 ppb. The question addressed in this study was whether all of this increase was due to the continued reaction of residual precursors with free chlorine or whether some of the increase was coming from reactions of free chlorine with material contained in the pipe deposits within the distribution system. In other words, is deposited material within the pipes of a distribution system a precursor for the haloform reaction. While most of this material is calcium carbonate, the actual composition is likely to be considerably more complex. Since little work had been reported on the characterization of these materials, it was felt that the possibility of the presence of precursors deserved investigation.

Both laboratory and field studies were conducted in an effort to verify the presence of precursors in pipe deposits. In the first approach, a section of pipe from the distribution system was secured and the deposit removed and studied for THM production. The second approach consisted of a field study of an unused, dead end section of water main. Details of the procedures used are found on pp. 21-23.

Results of the laboratory studies are shown in Figure 5. As indicated, the chloroform concentration increased with the amount of pipe material, which ranged from 0.10 to 1.0 g per 300 ml of solution. The chlorine dose (3.43 ppm) was approximately the same as in the distribution system, however, the pH (at 11) was not. While the formation of chloroform in increasing amounts cannot be directly related to observed increases in the distribution system the results do verify the presence of precursor material in the pipe deposit. Whether these precursors are organic species adsorbed

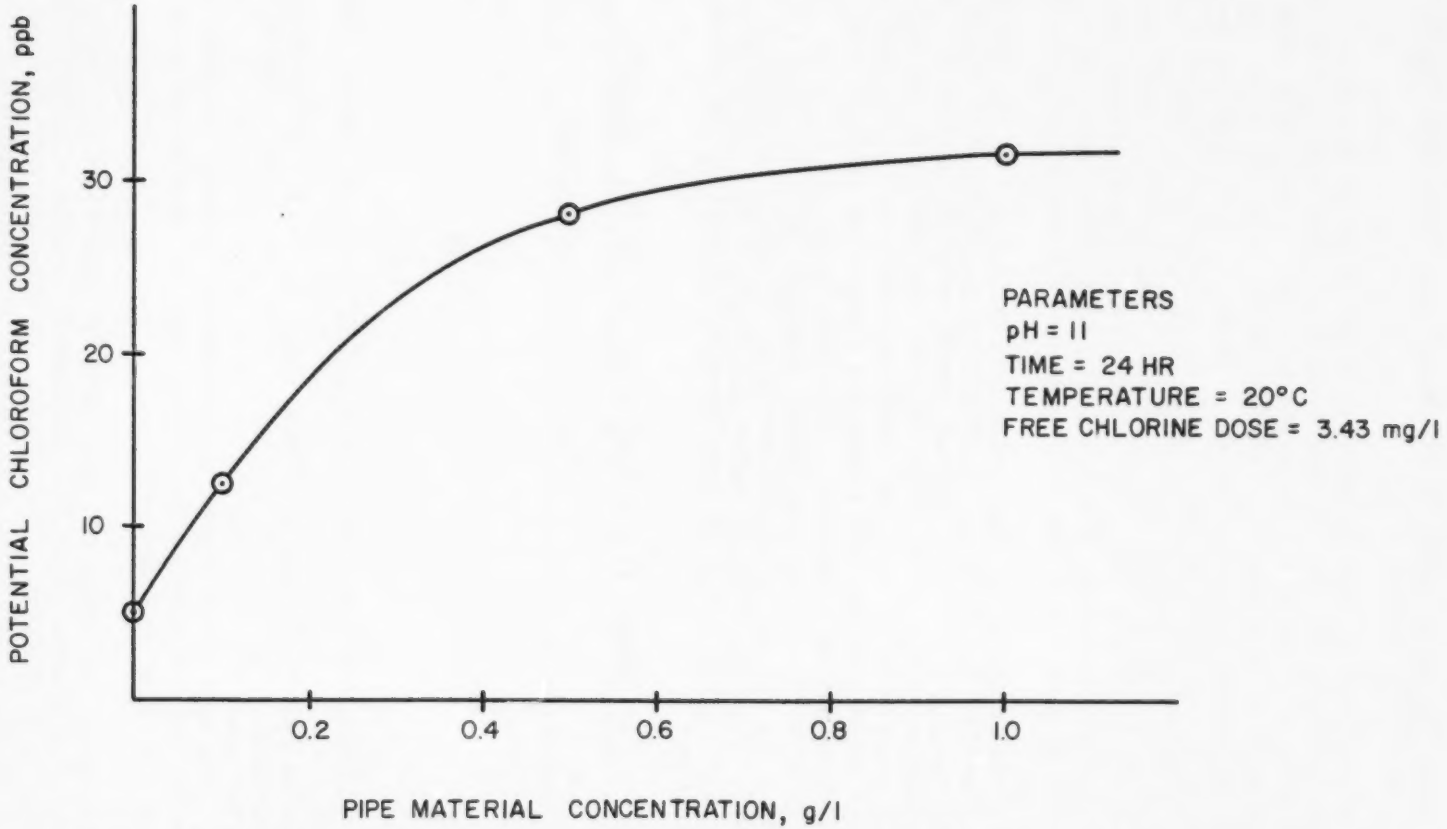

Figure 5. Potential chloroform concentration from pipe material at a chlorine dose of 3.43 mg/l.

from the water onto the pipe material, or whether the precursors result from some sort of growth is not known.

Results of a second, similar laboratory study in which the chlorine dose was 18.2 ppm and the pipe material ranged from 5.0 to 200 g per 300 ml of solution are shown in Figure 6. In contrast with the first study, here an inverse relationship is observed, i.e. the chloroform concentration decreased as the dose of pipe material was increased. Free and total chlorine determinations on the solutions at the end of the test indicated that all the reactions were chlorine limited. Just the opposite had been true for the first study. It is presumed that the decrease in chloroform concentration with increasing levels of pipe material results from competing reactions for the chlorine, i.e. non-precursor organics are successfully competing for the chlorine, leaving progressively less for reaction with the actual precursors.

While these tests did prove the presence of precursors in the pipeline deposits, the contribution of these precursors to the observed increase in THM concentrations within the distribution system remained uncertain. Both the physical characteristics of the pipe deposits and the pH of the solution were considerably different from actual pipeline conditions. In addition, results of total organic carbon (TOC) determinations (see Table 5) indicated that the James River was very stagnant. According to Dr. O. T. Love, Jr., these TOC values were reportedly the highest observed for a drinking water (to that date) by the EPA Municipal Environmental Research Laboratory, Cincinnati, Ohio. Even the finished water was found to have a TOC value of 1.6 ppm, which could account for the considerable "growth" of THM within the distribution system.

TABLE 5. TOTAL ORGANIC CARBON CONCENTRATIONS ON FEB. 14, 1978

Location	Total Organic Carbon, mg/l
Raw Water	21.81
Clear Well	1.58
Airport	1.81

Following the laboratory test, a field study was conducted in an attempt to evaluate the actual contribution of the pipeline precursors. The test developed and performed was referred to as the "In Pipe Test" and is outlined on p 23. The test was designed to compare the "growth" of chloroform in a quarter mile dead end main at Huron with baseline samples collected from the same main but free of pipe deposits.

The main selected for study had been idle for several months and presented a number of problems. Even with prolonged flushing, the baseline samples contained some deposits. In addition the pipeline was depleted of chlorine within 48 hours indicating the presence of considerable oxidizable

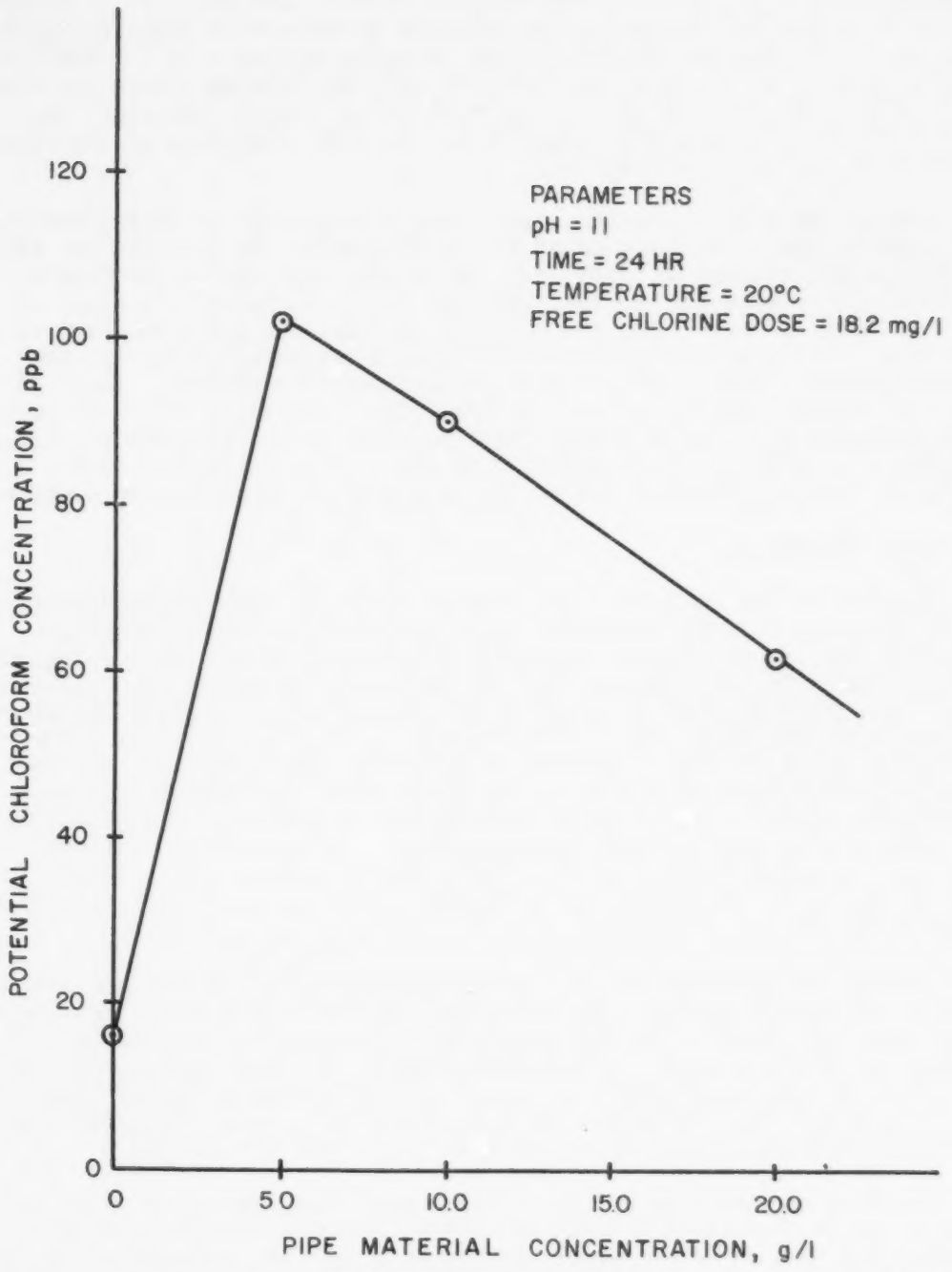

Figure 6. Potential chloroform concentration from pipe material at a chlorine dose of 18.2 mg/l.

material. Within the 48 hours the baseline samples were found to be slightly higher in chloroform concentrations than the corresponding pipeline samples. This was likely due both to the greater chlorine residuals of the baseline samples as well as to competing reactions for the chlorine within the pipeline (similar to those observed for the chlorine limited laboratory test). Such reactions are certainly suggested by the rapid depletion of the chlorine relative to the baseline samples.

Due to the problems encountered in the first series of tests, the study was repeated following a period of time during which the line was put back in service and allowed to stabilize. An attempt was made to reschedule the study at a time when the residual chlorine level was relatively high. In spite of these preparations, the chlorine residual was again depleted within 48 hours. This time no significant difference was observed between the chloroform concentration of the pipeline and baseline samples. Thus, while the experimental conditions were far from ideal, leaving a number of questions unanswered, it would appear that the contribution from the pipeline precursors is minimal in comparison with that of the residual precursors in the water itself. This may not be the case with all distribution systems.

Raw Water Parameters

Because of the low levels and complex nature of the THM precursors, it is difficult to directly determine their concentration and corresponding potential for THM formation. Potential THM determinations require the use of fairly complex instrumentation, skilled laboratory personnel and considerable time. Some work has been reported on attempts to relate certain raw water parameters to the potential for THM formation. Such correlations not only provide a simpler means of monitoring potential THM levels, but can also provide insight into the source of the precursors. Throughout the course of the project a number of raw water parameters were monitored and evaluated for correlation with observed THM concentrations. The parameters monitored included pH, temperature, specific conductance, chemical oxygen demand, total residual suspended solids, volatile suspended solids, ammonia, turbidity and chlorine demand.

During the course of the monitoring, the Huron treatment plant underwent a number of changes as their new plant was put into operation. These changes were often reflected in the THM levels and as such complicated the efforts of finding correlations with raw water parameters. Stagnant river conditions and low river flow (reflecting the previous years drought) further complicated these efforts. These factors were undoubtedly responsible for much of the poor correlation observed for most of the parameters studied.

In order to correlate raw water parameters with THM formation, a new test was devised to measure what was termed "potential trihalomethanes" (PTHM). The details of the procedure for this test are presented on p. 22. Basically the test was designed to evaluate the concentration of THMs that could result from treatment (of the test water) at prescribed conditions of pH and chlorine does. A pH of 11, approximating that of lime softened water, was selected. Incubations were for 72 hours at 20°C. It was desirable that

the reaction not be chlorine limited, i.e. that the results reflect a total potential THM concentration. In order to select an appropriate chlorine dose for such a test it was first necessary to evaluate the effect of chlorine dose on the THM production of a representative sample. Initial test were found to be chlorine limited and resulted in THM levels which were directly proportional to the chlorine dose. This emphasized the importance of assuring that the chlorine dose be in excess, for each time a set of samples was collected for the study of raw water parameters, it was necessary to prepare fresh chlorine water and the concentrations of these solutions varied somewhat. Fig. 7 gives the results of a test in which conditions varied from chlorine limited to precursor limited. Here the THM concentrations increase with chlorine dose up to a point and then level off. This allows selection of the minimum chlorine dose to assure an excess of chlorine. Fig. 7 also indicates that THM concentrations are chlorine dependent under chlorine limiting conditions.

Once a chlorine dose had been selected, correlation between THM levels and raw water parameters were studied. Of these parameters only temperature, specific conductance and turbidity showed good correlation.

Temperature. The effect of temperature, a parameter known to affect THM production, is shown in Fig. 8. Much of the scattering of points is presumed to be due to uncontrolled variations in other parameters which affect THM formation. Laboratory studies on the affect of temperature on THM growth curves indicate that while the rate of formation is proportional to temperature, given sufficient time, (36-48 hours) the final concentrations will be approximately the same. Fig. 9 shows this effect.

Specific Conductance. Good correlation was observed between specific conductance and potential chloroform levels. The results, as shown in Fig. 10, indicate that the potential chloroform concentration increases with increasing specific conductance. This indicates that a good portion of the precursors are in solution in an ionic state, as would be expected for humic acid type substance. This is also in agreement with results of growth curve studies which indicate that THM concentrations do not increase linearly with pH, but rather that there is a pH above which THM formation is significantly enhanced (see Fig. 11). This suggest the presence of ionizable acidic groups within the precursor molecules. Potentiometric titration curves generated on these solutions do not show any sharp breaks reflecting the specific pK values of the substances. This is not surprising in light of the complex nature of these compounds which undoubtedly vary considerably in their individual pK values.

Turbidity. A good correlation was also found between turbidity and PTHM levels. As indicated in Fig. 12, the more turbid the water the greater the THM concentrations. Since components of turbidity include finely divided organics, plankton and other organisms, either these, or their degradation products, must be precursors. While turbidity does not directly measure fulvic acid, it may do so indirectly since it is a degradation produce of plant material which does contribute to turbidity. No data was collected to correlate turbidity and natural color to supportthis possibility.

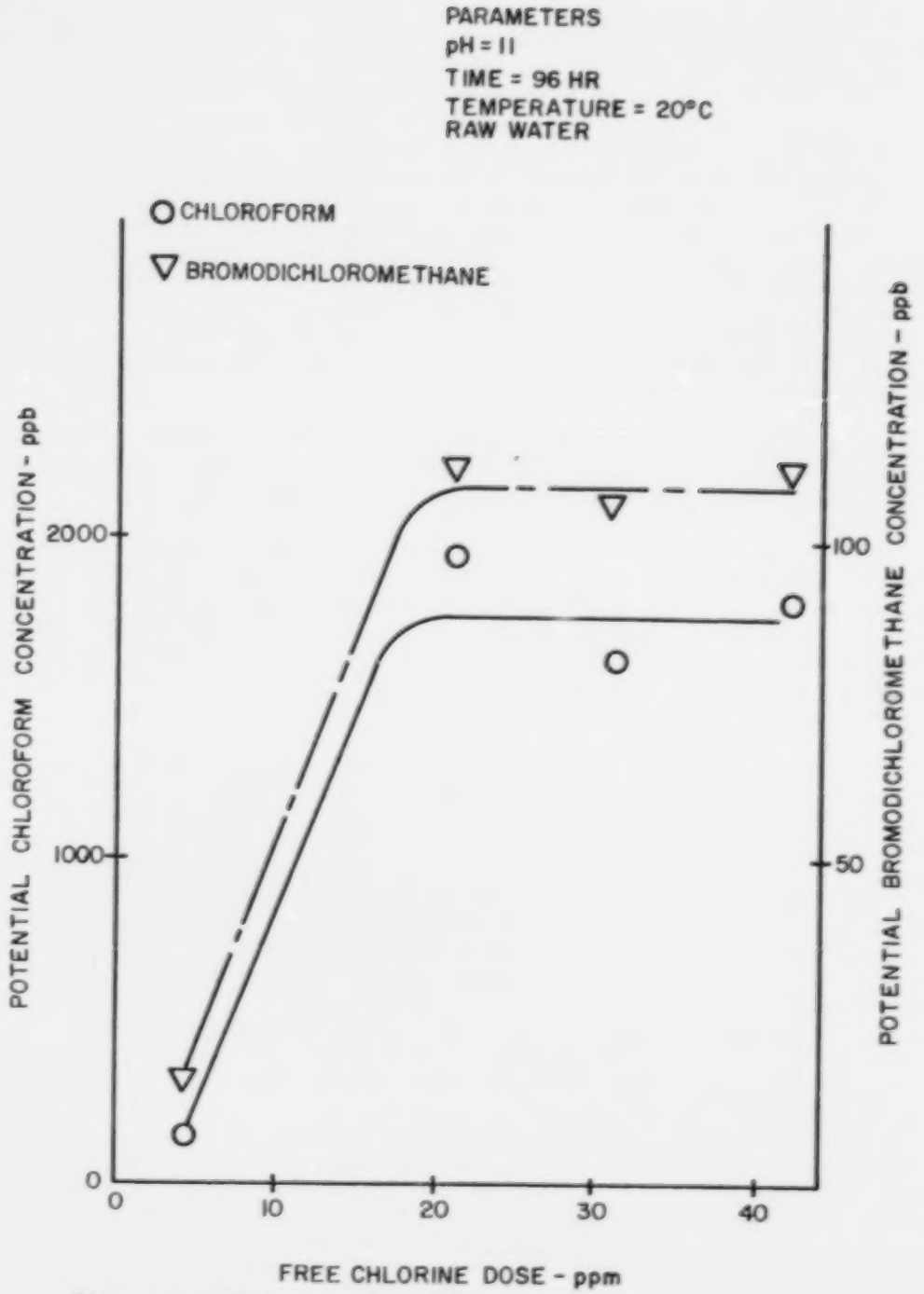

Figure 7. PTHM vs. Chlorine Dose (5/10/78).

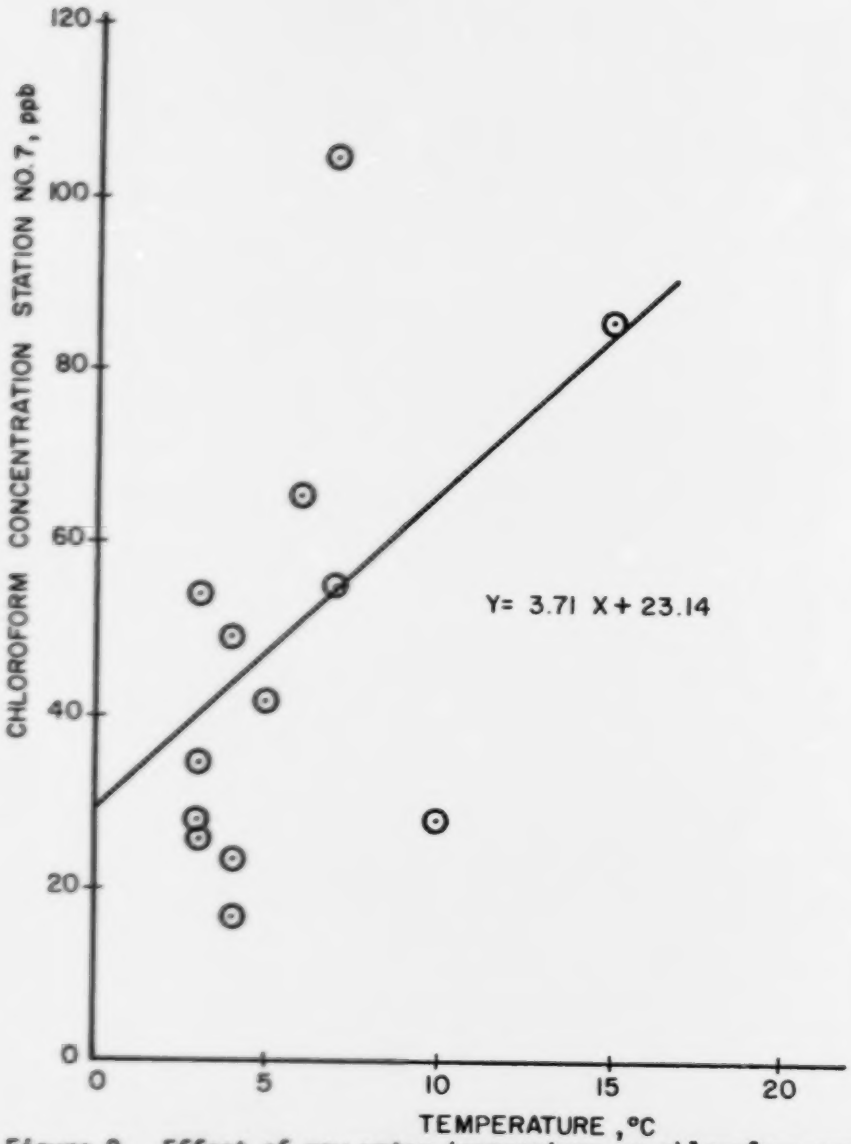

Figure 8. Effect of raw water temperature on chloroform concentration.

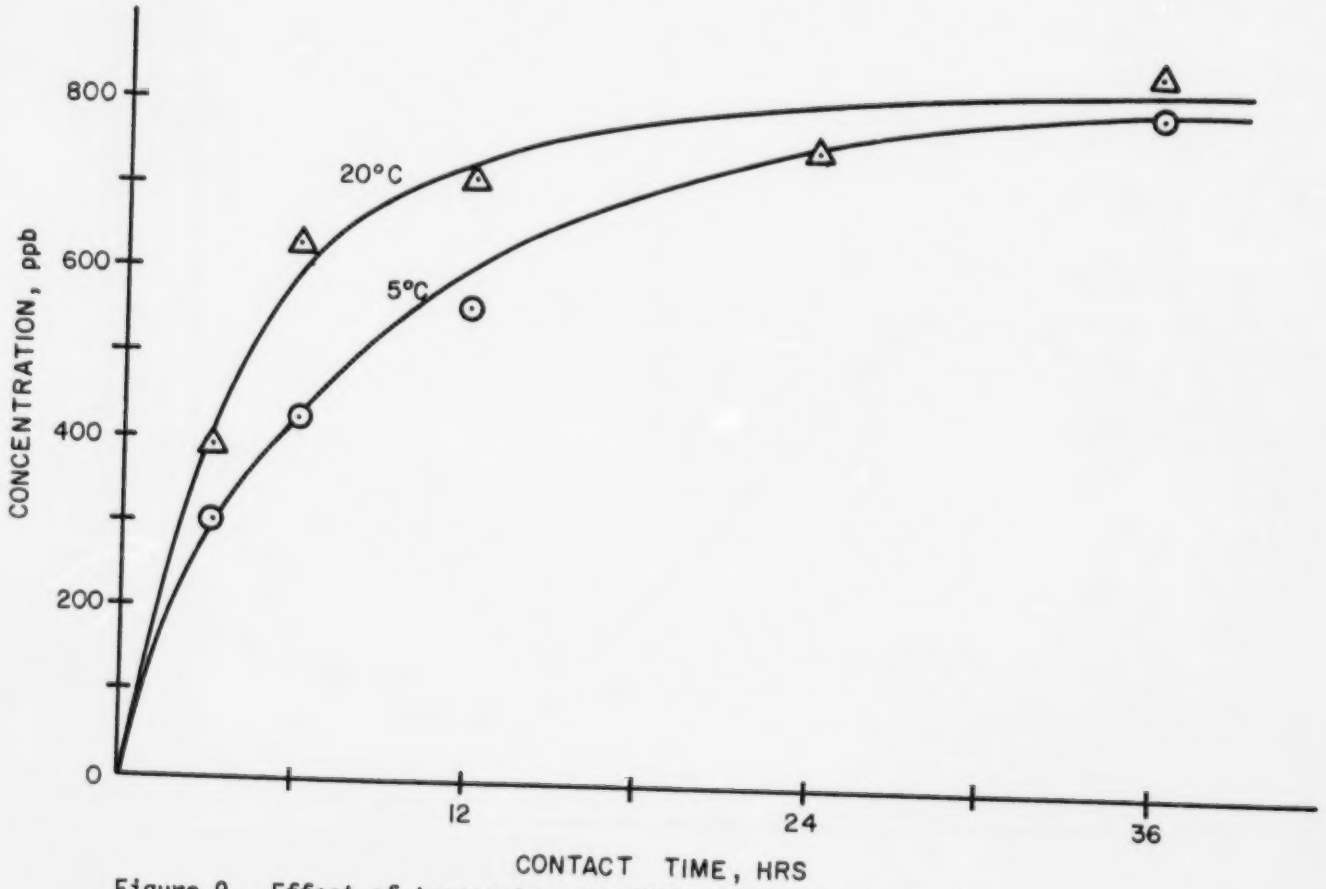

Figure 9. Effect of temperature on $CHCl_3$ formation at pH 11.

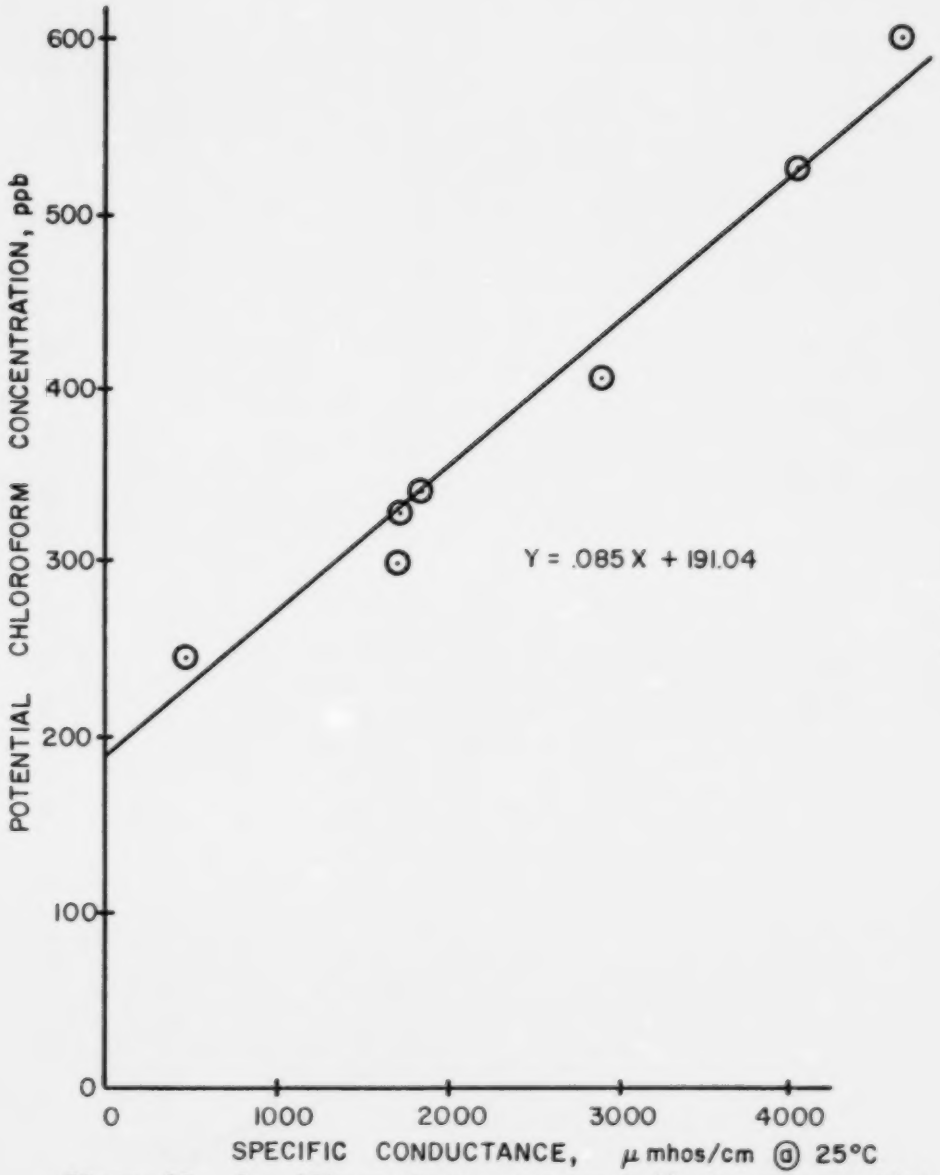

Figure 10. Specific conductance as an indicator of potential chloroform concentration.

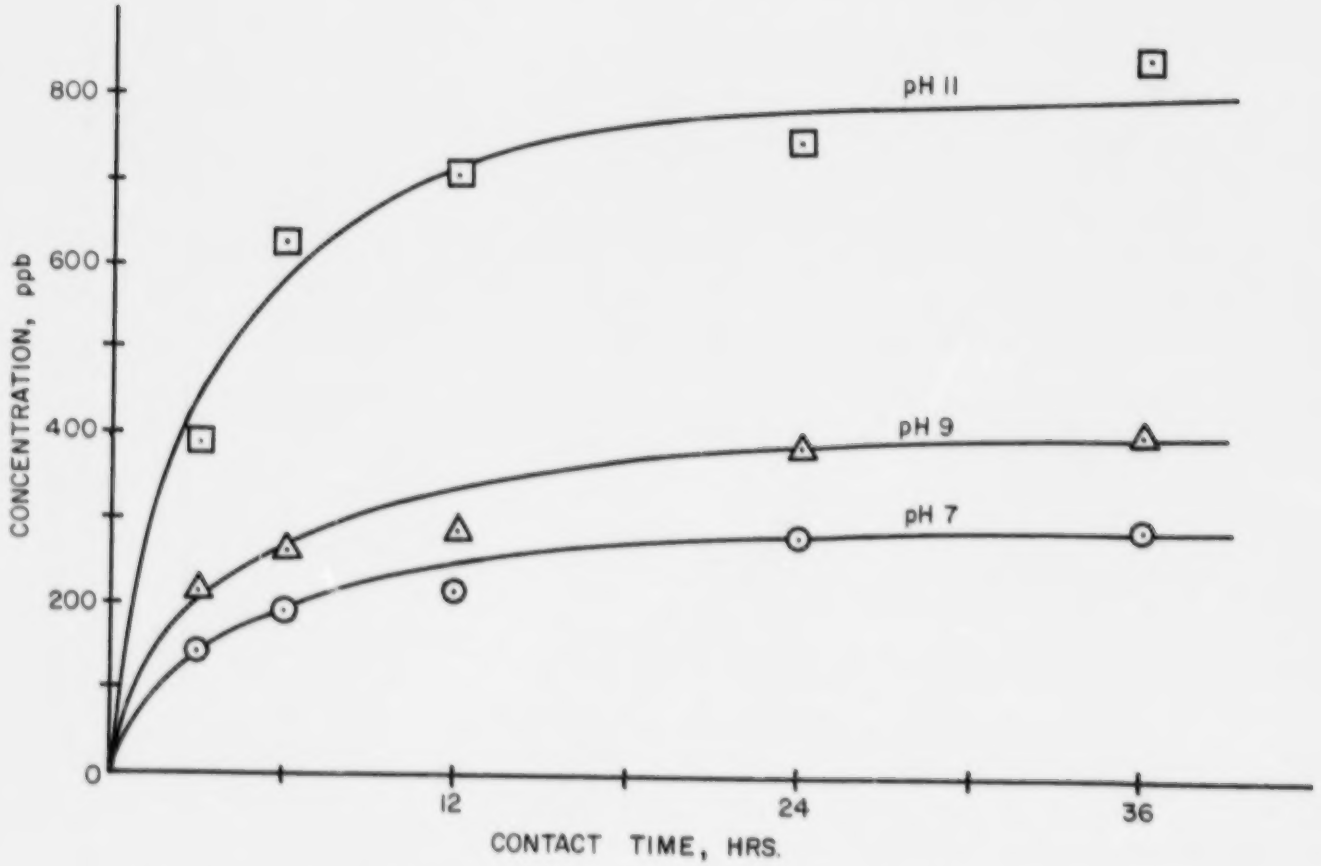

Figure 11. Effect of time and pH on $CHCl_3$ formation at 20°C.

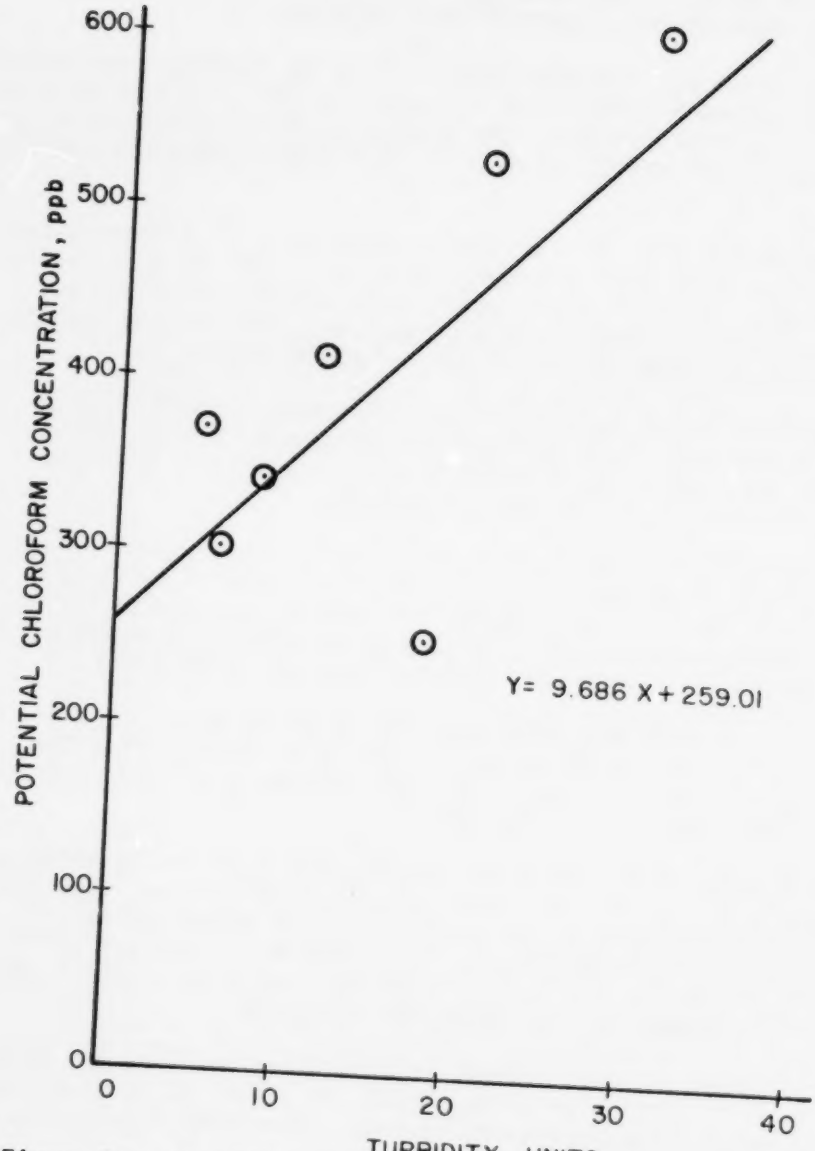

Figure 12. Turbidity as an indicator of chloroform concentration.

Land Use. The James River was a stagnant pool of water for most of this study. Flow was recorded during the last three months of the year that monitoring was conducted. While this severly curtailed land use studies, a study was made along a twenty-eight mile section of the river starting at the James Diversion Dam north of Huron. Samples were collected at key locations along the 28 mile span and studied for potential THM formation.

Results of the survey are presented in Fig. 13. As indicated the potential chloroform concentration varied from a low of 706 ppb to a high of 3300 ppb. The high concentrations reflected the stagnant conditions of the river. In addition the samples were overdosed with chlorine which drove the reaction to the extreme.

It can be noticed from Fig. 13 that the chloroform level reaches a peak about 15 miles upstream from Huron and then decreases. Some of these values seem unreasonably high. However, there is no known analytical reason for disregarding these data. All samples were treated the same and the results do reflect differences in water quality at the sampling sites.

When comparing land use to potential chloroform concentration, three general trends were observed. Peak concentrations seemed to occur where marsh flow ran into the river, where cattle were watering along the river bank, and where the river was very broad and shallow.

It was not surprising to find a high potential for chloroform formation in the marsh areas since these are an excellent source of fulvic and humic acid substances. To test this theory an oxbow marsh south of Huron Colony, S.D., was located and tested. The potential chloroform concentration of this sample was 27% higher than samples from the James River.

High chloroform potential was also found in locations where cattle watered. While this increase would be mainly due to precursors from the cattle excretions, a second factor could be the stirring up of the river bed with the release of degraded plant material.

The increase in potential chloroform concentrations at the location where the river was very shallow could have several explanations. The biota could well be quite different, e.g. reflecting a higher temperature; organics could be easily released from the river bottom under windy conditions, such as were present at the time of sampling; and finally there were cattle tracks present, suggesting contamination by cattle.

Seasonal Variations. Also considered in the context of land use were seasonal variations. Of particular interest was the effect of agricultural runoff which would be reflected in seasonal trends. Municipal discharges, however, would be diluted by high runoff.

As previously mentioned, this study began during a period of drought. There was no flow in the James River from October, 1977 to March, 1978. During this time little change was observed in the PTHM levels. By March 10, 1978, spring runoff sustained flow in the river and the PTHM levels began to increase. The monitoring data are summarized in Fig. 14. The substantial

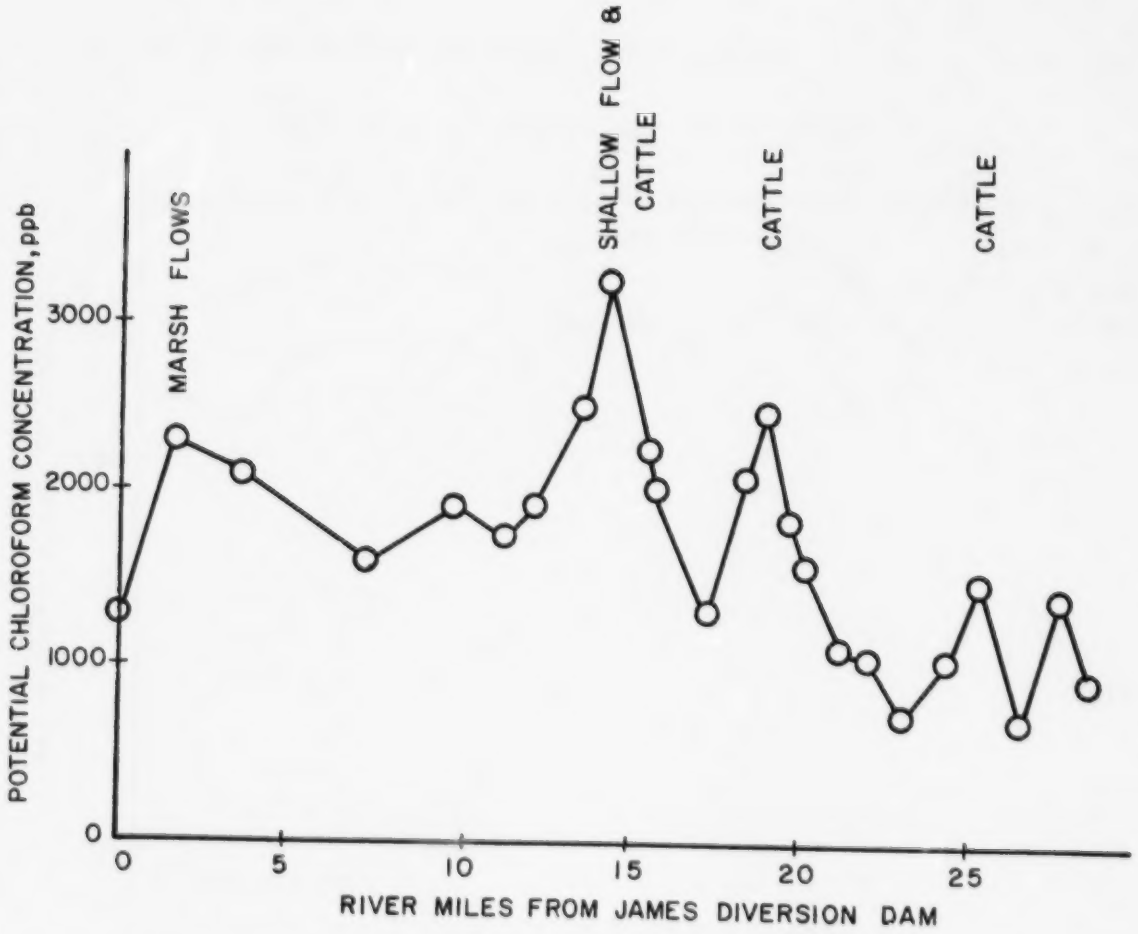

Figure 13. Potential chloroform formation within the James River.

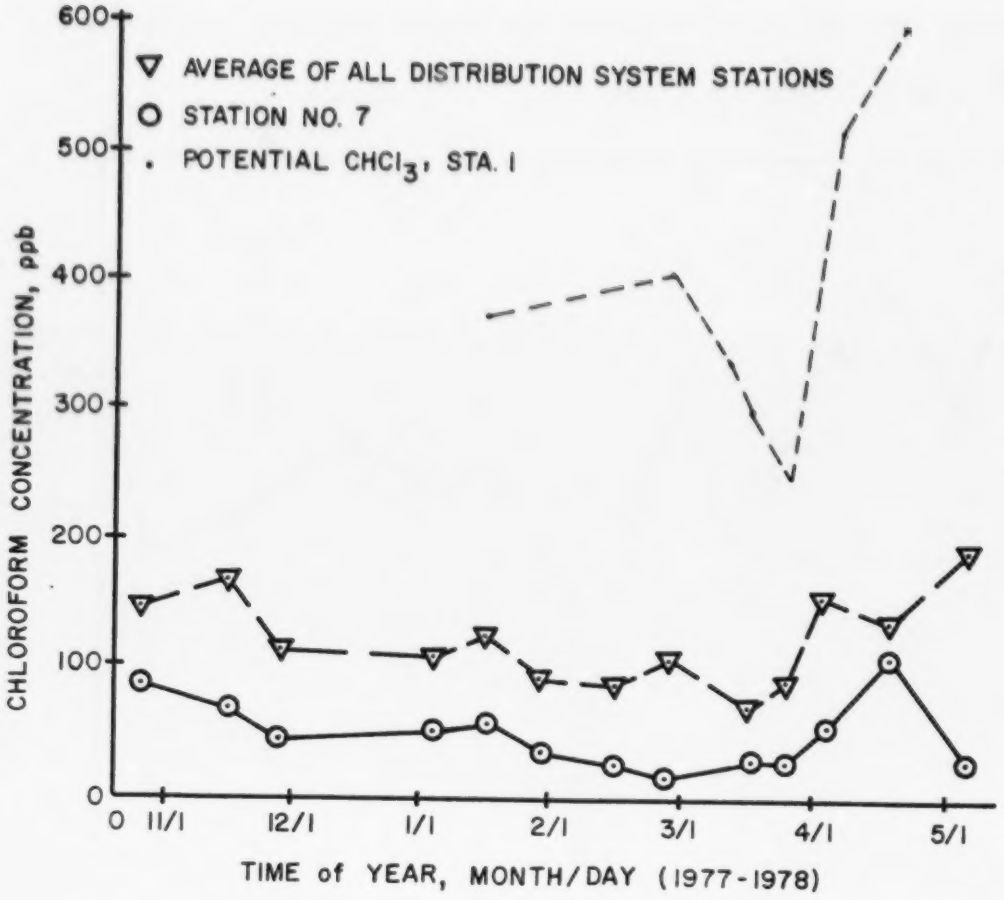

Figure 14. Variation of chloroform concentration.

increase in THM concentrations following the spring runoff supports the theory that organic precursors are leached from the soil during periods of heavy rainfall and runoff. High flow rates could also stir up organics from the river bed which could also account for the increases observed.

Interestingly, the concentration of bromodichloromethane (BDCM), decreased as the flow rate increased. Data are summarized in Fig. 15. The decrease in BDCM concentration began following March 10, the day flow began in the river, and reached a minimum on April 4, the day on which maximum flow was recorded. This indicates that agricultural runoff is not a significant source of bromide. On the other hand, bromide from other sources, such as municipal discharges, would be diluted by the runoff.

Monitoring Trihalomethanes

Throughout the duration of the project, THM concentrations were monitored both in the water treatment plant and in the distribution system. (Complete data for the monitoring are contained in the Appendix). Results of previous work at Huron (2) had indicated the importance of pH and therefore the significance of the location of the point of prechlorination. At the start of the current project, prechlorination was still positioned at the recarbonation basin, to which it had been moved during the previous work. Chloroform concentrations in the plant effluent (clearwell) were at about 40 ppb. In August prechlorination was moved back to station 3, the point of lime addition and maximum pH. The change was made in an attempt to combat taste and odor problems that were being encountered in treating the stagnant water supply. Following the change, THM were observed at stations 3 through 7. Slight increases at station 7 reflected postchlorination.

The point of prechlorination was returned to the recarbonation basin on start-up and samples collected on February 27, 1978 showed a significant reduction in $CHCl_3$ throughout the treatment plant. While the plant effluent levels were reduced, concentrations in the distribution system remained relatively unchanged. Figures 14 and 15 summarize the data for both the plant effluent and the distribution system.

Disinfection with pH

It is well known that microorganisms prefer a certain pH range for growth. Consequently exposure to an adverse pH can result in the destruction of the cell. Most bacteria have an optimum growth rate near pH 7, and do not tolerate high pH values for extended periods of time (See Table 6).

The water softening process at Huron uses lime which results in a pH near eleven for a period of about 3.5 hours. Because alternate methods of disinfection were being considered, especially the use of combined chlorine, it became important to better define the disinfection which occurred as a result of the conventional water treatment processes, including lime softening. Disinfection which occurs at high pH levels may or may not

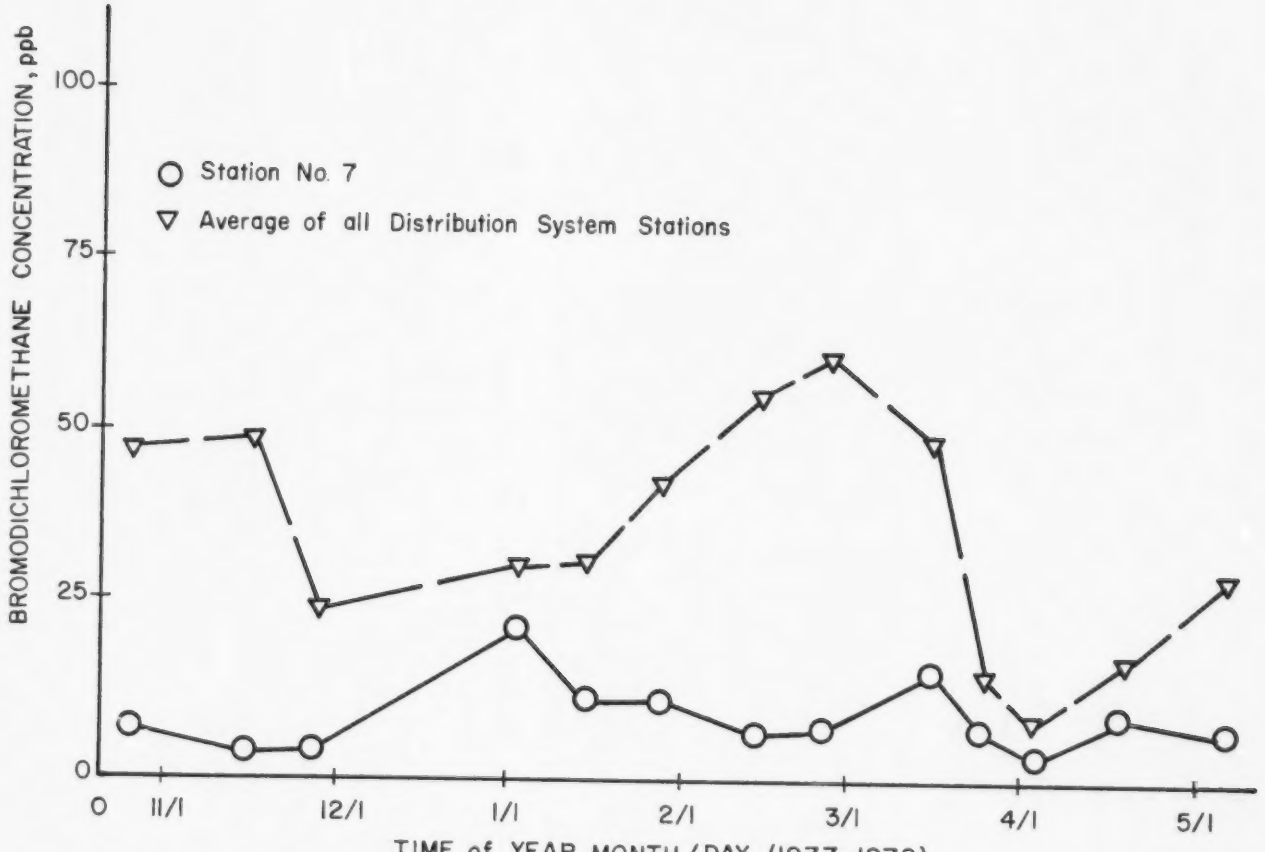

Figure 15. Variation of bromodichloromethane concentration.

TABLE 6. OPTIMUM pH RANGES FOR SOME COMMON BACTERIA (16)

Bacteria	Minimum pH	Growth Range	Maximum pH
Escherichia coli	4.4	6.0-7.0	9.0
Salmonella typhose	4.5	6.5-7.2	8.0
Corynebacterium diphtheriae	6.0	7.3-7.6	8.3
Neisseri gonorrhoeae	5.8	6.8-7.4	8.2

qualify as a primary disinfectant as defined by EPA (8) in the proposed amendment to the drinking water regulations. If adopted as proposed, the regulations would not allow the use of combined chlorine unless another primary disinfectant had already been used. The amendment also states that: "Chloramines shall not be utilized as the primary disinfectant in drinking water. Chloramines may be added for the purpose of maintenance of an active chlorine residual in the distribution system only to water that already meets primary drinking water regulations."

A laboratory study to determine the effect of pH on total coliforms was performed in duplicate with a water sample from the presedimentation basin effluent (Sta. 2). The initial bacterial count averaged 12,700 total coliforms/100 ml. Four different sub-samples were also taken and adjusted to pH ranges of 8, 9, 10, and 11 respectively. Total coliform tests were run at 15, 30, 60, 120, and 240 minutes on each sub-sample. These data are presented in Fig. 16. The data show a general bacterial decrease as the pH increases, with pH 11 being the most pronounced.

This laboratory study indicated that pH inhibits bacterial survival, and at the in-plant pH and contact time one could expect complete destruction of coliforms. To further determine the influence of pH, an in-plant study was performed for two months. Total coliform samples were taken at the presedimentation basin effluent (station 2N), which is immediately before lime softening. Another sample was taken immediately after lime softening (station 5N) and was neutralized at the time of sampling. The difference in bacterial counts between station 2N and 5N will show the effect of pH. The data (see Table 7) shows an average reduction in total coliforms of 93%. The average detention time (based on a 2750 gpm flow) read about 1.2 hours at the resulting high pH during the time these data were collected.

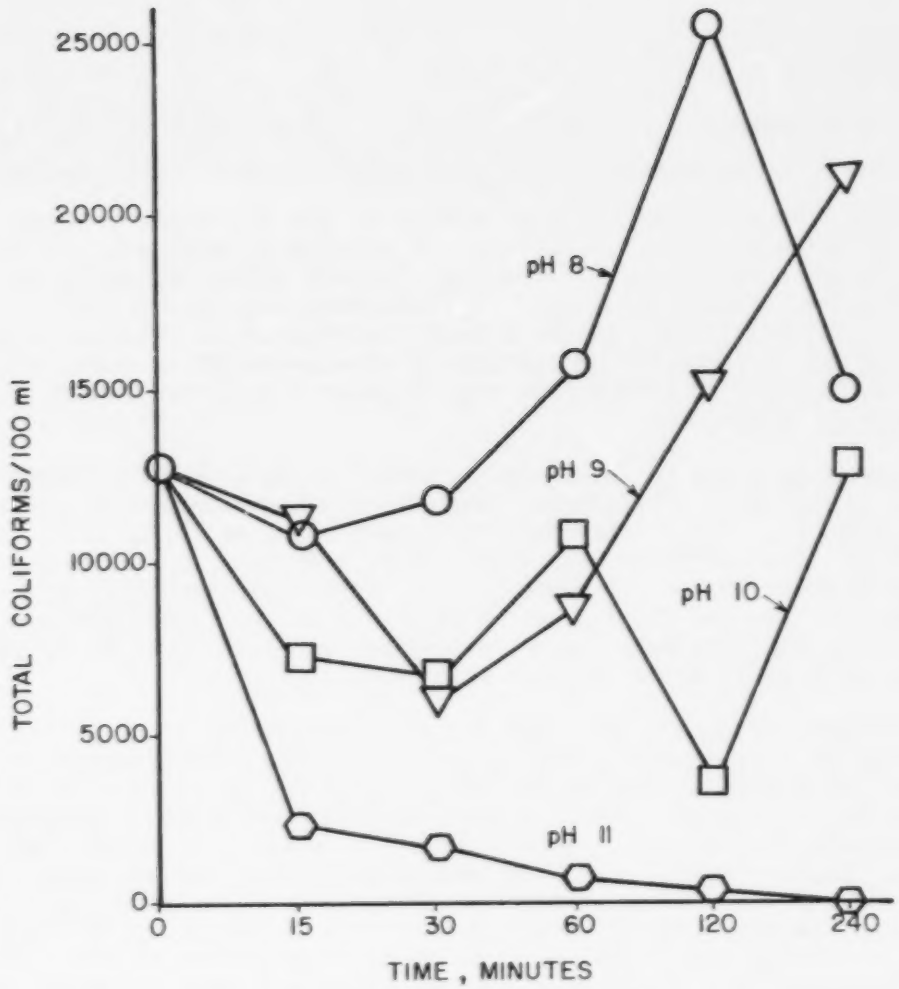

Figure 16. Coliform disinfection by pH.

TABLE 7. REDUCTION IN TOTAL COLIFORMS FROM STATION 2N TO STATION 5N DUE TO LIME SOFTENING

Date	Station 2N Total Coliform 100 ml/	Station 5N Total Coliform 100 ml	pH	% Reduction
2/21/78	15,000	8	10.7	99
2/29/78	400	7		98
3/10/78	273			
3/15/78	692	17	11.2	97
3/25/78	116	4	10.6	96
3/28/78	15	0	11.2	100
4/ 4/78	310	23	11.2	92
4/10/78	50	3	11.0	94
4/19/78	330	104	10.3	68

The above results clearly show the effect of high pH on bacterial survival. It should be noted that fecal coliforms were seldom run on bacteria samples. One reason is the high turbidity of Huron's raw water limits the quantity of sample that can be filtered. If an inadequate amount of water is filtered, an unrepresentative sample is obtained. Another reason is the fecal coliform population in the partially processed water is almost zero. This correlates with the low total coliform counts at these stations.

Four total coliform tests were run over a 1.25 hour period to determine the uniformity of Huron's raw water. The tests showed a range of 5,800 - 17,800 total coliforms/100 ml with an average of 12,625 per 100 ml. The results indicate an extremely variable water.

On the same day, a similar test was run at Station 5N. Values ranged from 10-65 total coliforms/100 ml with an average of 34 per 100 ml. This indicates a more uniform water because the presedimentation basins and softening basins allow for mixing. These data also show the effect of settling and lime softening on bacteria. A 99% reduction in total coliforms was obtained.

Two additional laboratory experiments were conducted in duplicate using two pathogens, Salmonella typhi and Salmonella typhimurium. In the first experiment, known titers of approximately 100 cells/ml of each pathogen were placed in presterilized water from the Huron water treatment plant. The limed water had a pH of 10.8. After 2 hours contact time the samples were incubated on BHI agar plates and counted for colonies. Results are shown in Table 8. Neither of the pathogens were able to survive for even two hours in the water from the Huron water treatment plant.

In the second experiment, the titer was raised to 1,000 cells/ml of S. typhi and S. typhimurium. Cells were placed in 0%, 25%, 50%, 75%, and

TABLE 8. INCUBATION OF 100 CELLS/ml OF PATHOGENS IN LIMED WATER

Percent Limed Water	Dilution	No. of Cells/100 ml	
		S. Typhi	S. Typhimurium
100	1:1	0, 0	0, 0
	1:10	0, 0	0, 0
	1:100	0, 0	0, 0
50	1:1	0, 0	0, 0
	1:10	0, 0	0, 0
	1:100	0, 0	0, 0
25	1:1	8, 12	11, 0
	1:10	1, 0	1, 0
	1:100	1, 0	1, 0
0	1:1	84, 80	130, 85

100% limed water from Huron and allowed to set for two hours. Double strength BHI was added to the samples which were then incubated and confirmed on triple sugar iron agar slants. Sample results were recorded as positive (Salmonella survived) or negative (Salmonella destroyed). Results indicate that survival was only possible for either species if the limed water was diluted (See Table 9).

TABLE 9. INCUBATION OF 1,000 CELLS/ml OF PATHOGENS IN LIMED WATER

Percentage of Limed Water	S. Typhi	S. Typhimurium	S. Typhi	S. Typhimurium
0%	+;+	+;+	+;-	+;-
25%	+;+	+;+	+;-	-;-
50%	-;-	-;-	-;-	+;-
75%	-;-	-;-	+;-	-;-
100%	-;-	-;-	-;-	-;-

+ = Growth
- = No Growth

Results of the bacterial testing with pH as the variable reinforced the concept of using combined chlorine for disinfection at Huron. It appeared that most of the micro-organisms were inactivated from the pH used in the treatment process, and the main purpose of the disinfectant used was to prevent contamination from occurring after the water entered the distribution system.

Previous Experience Using Combined Chlorine

Race (9) was the first to use combined chlorine as a disinfectant. Until that time (1916), chlorination was accomplished by using free chlorine. Race reported that using hypochlorite produced a water without taste or odor. Combined chlorine use reached a peak between 1929 and 1939 because of research by McAmis, Lawrence, and Braidech (10) which showed taste and odor control with combined chlorine. However, Griffin (10) discovered breakpoint chlorination in 1939 and soon water treatment plants were changing to free chlorine for better disinfection.

Several early investigators indicated that free chlorine was a better disinfectant than combined chlorine. Howerda (10), Butterfield (11), and Wattie (10) contributed to this work. The consensus was that combined chlorine required 100 times more detention time than when using free chlorine or a concentration 25 times that of free chlorine (10).

Clarke et al. (10) in 1962 composited and evaluated previous data to prepare curves of germicidal efficiency of different chlorine residuals (see Fig. 17). This yielded a common base to compare the disinfection efficiencies of free chlorine (HOCl, OCl^-) and combined chlorine (NH_2Cl).

The difference in germicidal effectiveness between free chlorine and combined chlorine decreases at higher pH values. At pH 9 and 20°C, slightly over 97% of the free chlorine is in the OCl^- ion form. The OCl^- ion is a much poorer disinfectant than hypochlorous acid (HOCl). Figure 17 illustrates that the effectiveness of the OCl^- ion and monochloramine is similar. In fact, White (10) states that the chloramines are better cysticidal agents at pH values of 9 and above. This fact should be remembered when disinfection effectiveness is discussed, especially at treatment plants where the effluent pH is about 9. Lime softening plants in the upper midwest frequently have pH values in this range.

Several advantages of using chloramines for disinfection have been recognized for several years. Those reported by Babbitt (12) include:

(1) Prevention of tastes, especially phenols.

(2) Control of microorganisms in settling basins, filters, and distribution systems because heavier chlorine dosages will not result in taste problems.

(3) Stronger bactericidal effects than with free chlorine only when substantial organic matter is present.

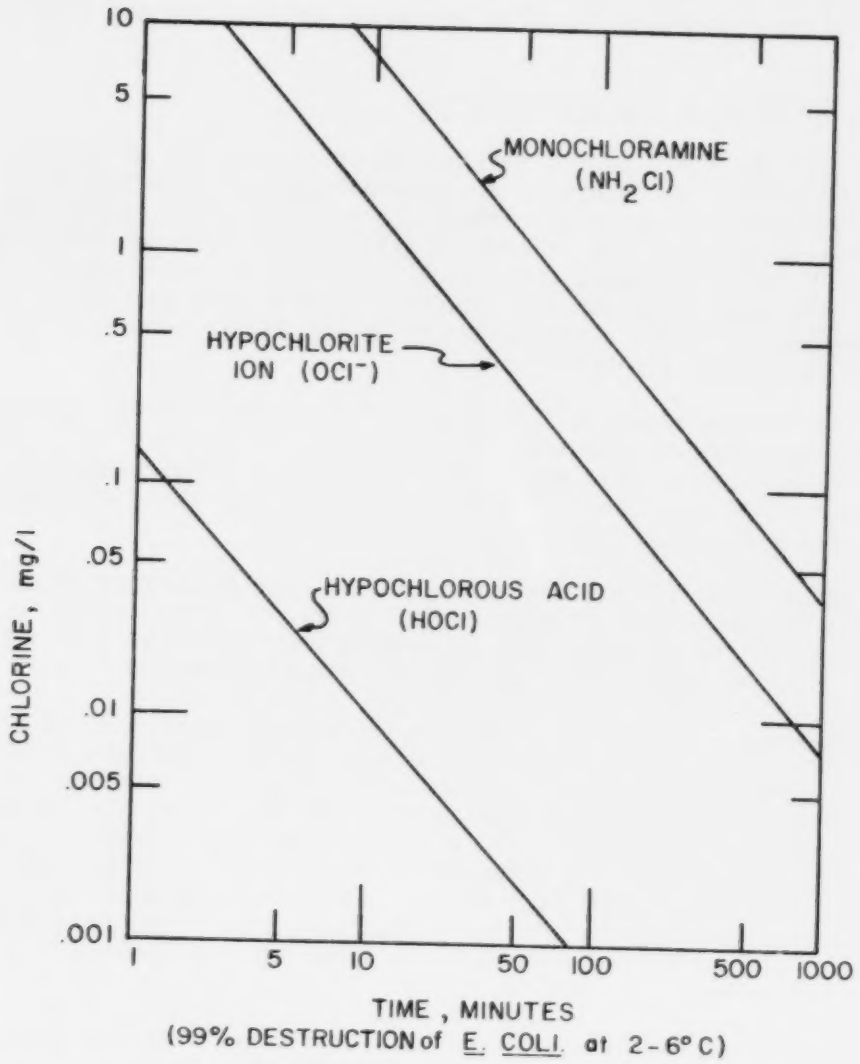

Figure 17. Comparison of germicidal efficiency of hypochlorous acid, hypochlorite ion, and monochloramine, after Clark et al. (10).

(4) Long residuals for inhibition of after-growths.

(5) Reduction of chlorine requirements.

(6) Adequate dosages for no fear of overdosing.

(7) Freedom from danger, since chloramines are nontoxic.

(8) A high degree of stability.

Disadvantages of disinfection by using combined chlorine are:

(1) Longer detention times for adequate bacterial control than when free chlorine is used.

(2) Contact time for chlorine and ammonia to convert to chloramines.

(3) An initial investment for ammoniation is required.

(4) Maintaining a correct chlorine:ammonia-nitrogen ratio to prevent taste and odor problems from dichloramine and trichloramine formation.

(5) Its ineffectiveness against viruses (13).

In 1963, 308 water treatment plants of the 11,590 treatment plants in the United States reported using chloramines as a disinfectant. This small percentage reveals that chloramine disinfectant can be effective and reliable. Some of the major plants still using chloramines are St. Louis, Missouri; Kansas City, Kansas; Denver, Colorado; and Pueblo, Colorado. Jefferson Parish in Louisiana has used chloramine disinfectant for the past twenty years with great success. Bacteriological field samples have been satisfactory at all times. (Personal communication, N. Brodtman, Supt. Jefferson Parish Water Treatment Plant).

Chicago (13) recently switched from combined chlorine disinfectant to free chlorine. Free chlorine resulted in a decrease in coliform density, but both types of disinfectant met health requirements. The mean coliform density for combined chlorine was 0.05 organisms/100 ml compared to 0.03 for free chlorine. More taste and odor complaints were reported when free chlorine was used. Also reported was the inability of free chlorine to maintain a chlorine residual throughout Chicago's 4000 miles of water mains.

Stevens (14) artificially spiked untreated Ohio River water with free and combined chlorine. At a 72 hour detention time the chlorinated sample had a total THM concentration of 160 ppb compared to 16 ppb for the combined chlorine sample. From this experiment, it is assumed THM concentrations leaving a water treatment plant will be similar to the THM levels reaching the consumer - if combined chlorine is used. Tuepker (14) showed this assumption to be correct in a study for the St. Louis County Water Company where chloramines are used for disinfection.

Ten of the eighty cities sampled in the NORS survey (1) used chloramines. The sum of the THM s in the chloramine systems ranged from 1 to 81 ppb with an average of 19 ppb. The total THM range for systems using free chlorine was 1 to 472 ppb with an average of 72 ppb. The high THM concentrations in some of the chloramine utilities are a result of free chlorine being added prior to ammoniating. For example, the Kansas City Water Works maintains a free residual for five hours before ammoniating and their total THM concentration was only 34 ppb in the NORS survey. The St. Louis Water Company softens and chlorinates and allows eight hours before ammoniating. Their five month average chloroform concentration was 49 ppb (14).

It appears that the use of combined chlorine as a disinfectant has some definite advantages, especially when trying to reduce the total trihalomethanes in a drinking water which has a high pH.

Kinetics of Chloramine Formation

The time involved for ammonia-nitrogen and free chlorine to form chloramines is important. As long as free chlorine is available, it has the potential to form trihalomethanes. The shorter the time that it takes free chlorine to combine with ammonia, the less chance for THM formation.

The formation of monochloramine is thought to occur as follows (15):

$$NH_3 + HOCl \rightarrow NH_2Cl + H_2O \qquad \text{EQN 2}$$

OR

$$NH_4^+ + OCl^- \rightarrow NH_2Cl + H_2O \qquad \text{EQN 3}$$

The equilibrium equation for ammonia is

$$NH_3 + H^+ \rightarrow NH_4^- \qquad \text{EQN 4}$$

with a high pH favoring the ammonia (NH_3). The equilibrium equation for free chlorine is

$$HOCl \rightarrow OCl^- + H^+ \qquad \text{EQN 5}$$

with a low pH favoring the hypochlorous acid (HOCl). For equation 2 to proceed a water with a high pH will have the ammonia available but is limited by the hypochlorous acid to form chloramines. A low pH will have the hypochlorous acid available but is limited by the ammonia. These same conditions also limit equation 3 for chloramine formation. Monochloramine is best formed at a pH of 8.3 with a chlorine: ammonia-nitrogen ratio of 5:1 or less by weight. Chloramines are about 100% pure dichloramines at pH of 4.5 to 5.5 and at a chlorine: ammonia-nitrogen ratio of 7:1 to 10:1, by weight.

White (10) states the optimum pH for chloramine formation to be 8.3 with a variance (either way) from this pH which increases the conversion time. He reports the conversion time for chloramine formation as 0.069 seconds at pH 8.3. It was not important to verify this information because the time frame for THM formation is based on minutes instead of seconds for the chloramine formation.

Several tests were performed to verify that the formation of chloramines does not take any appreciable amount of time. At pH 7.2, 99% conversion of chloramines was accomplished in six minutes; at pH 8.2, 98% conversion in twelve minutes; and at pH 10.8, 99% conversion in six minutes. It is known a 0.5 ppm concentration of free chlorine will promote THM formation (15). Thus a small amount of free chlorine can be a contributing factor for THM growth.

Simulation of Disinfection with Chloramines

Because the interim regulations from EPA proposed a THM limit of 100 ppb and would not allow the use of chloramines as a primary disinfectant, a disinfection procedure was experimented with which would use free chlorine as the primary disinfectant followed by chloramines. A tap was installed beneath the filters and ammonia and chlorine were added to filtered water to simulate chloramination after normal disinfection with free chlorine. Ten sample sets were taken over a two month period from beneath the filters with each set consisting of a dechlorinated sample, a sample spiked with chlorine, and a sample spiked with chlorine plus ammonia.

The dechlorinated sample was used to see the extent of THM formation which would occur from the primary disinfection with free chlorine. The sample which was spiked with chlorine was used to simulate THM concentrations which would be delivered to the consumer if final disinfection was continued with free chlorine. The remaining sample which was spiked with both ammonia and chlorine was used to determine what THM concentrations could be expected if the final chlorine dose was added as chloramines. These samples were dosed with the same chlorine dose that was being applied as the final dose at the water treatment plant. They were then allowed to set for two to eight days prior to testing to simulate detention time in the distribution system. Results are summarized in Table 10.

The results show a 55% reduction in TTHM concentrations by using chloramines instead of free chlorine. Free chlorine in the first four chlorinated samples was extremely small and this limited the THM concentration. Data from the last four sets of samples are somewhat misleading because the operators unintentionally changed the point of pH adjustment. This allowed the prechlorine dose to be added at a high pH which increased the THM concentration. Although a 55% reduction in TTHM concentration is significant, a greater reduction could have been observed if the above conditions would not have interfered.

The results also show the addition of ammonia did not stop the THM reaction entirely. A 317% increase in TTHM is observed from the dechlorinated to the chloraminated sample. The primary reason is suspected as being that the ammonia and chlorine were not immediately brought into contact with each other. The reagents were both added to a bubble-free 60 ml vial without physical mixing.

Throughout this same period of testing, aliquots from the dechlorinated sample and the chloraminated sample were tested for coliform bacteria. Coli-

TABLE 10. RESULTS OF CHLORAMINATION SIMULATION

Date	(1) Dechlorinated Sample TTHM (ppb)	(2) Sample plus Chlorine TTHM (ppb)	(3) Sample plus Chlorine and Ammonia TTHM (ppb)	Percent Reduction, Col. (2) to (3)	Percent Increase, Col. (1) to (3)
3/ 3/78	7	68	22	68	314
3/10/78	6	52	15	71	250
3/15/78	8	56	25	55	313
3/17/78	8	58	31	47	388
3/25/78	15	106	30	72	200
3/28/78	18	58	28	52	155
4/ 4/78*	15	199	123	38	820
4/10/78*	44	161	70	57	160
4/18/78*	38	102	55	46	145
4/24/78*	14	110	60	45	429

*Pre-chlorination at high pH

forms were not detected in any of the samples. From these results it appeared that adequate disinfection could be maintained within the distribution system while meeting EPA proposed regulations.

Start-up Using Combined Chlorine

Because of the initial favorable results regarding disinfection with chloramines and pH, it was decided to try combined chlorine disinfection at Huron. The consulting engineer in charge of the treatment plant expansion would not approve the installation of an ammoniator within the chlorination room. Financial considerations did not allow for construction of additional facilities, so it was decided to use dry ammonium sulfate powder as the source of ammonia. Some preliminary lab work confirmed that this approach was technically feasible.

A dry chemical feeder was located and used to meter ammonium sulfate into the effluent of the recarbonation basin (station 5.5N). This location allowed the mixing to occur hydraulically. The primary disinfectant, chlorine, was added in the recarbonation basin.

The initial start-up was concerned primarily with operating the ammonium sulfate feeder, determining chlorine residuals, and measuring the THM formed. Samples were taken at station 6N (over the filters) and at station 7 (clear well).

The first series of samples were collected at a 2.9 chlorine to ammonia-nitrogen ratio by weight (see Table 11). The chlorine dose was 220 pounds per day of chlorine and thus the feeder was to deliver 360 pounds per day of ammonium sulfate (76 pounds of ammonia-nitrogen). The instantaneous THM concentration was approximately the same as that of samples allowed to set for a four day period. The minimal increase in THM concentration during the four days is attributed to having had an excess of ammonia in the water (0.7 ppm ammonia-nitrogen).

The second series of samples were collected at a 4.5 chlorine to ammonia-nitrogen ratio by weight. Consequently the ammoniator was reduced to 230 pounds per day of ammonium sulfate (50 pounds of ammonia-nitrogen). The instantaneous THM concentrations (Table 11) are the same as the 2.9 chlorine: ammonia-nitrogen ratio by weight; however, because excess ammonia was not available (less than 0.1 ppm ammonia-nitrogen) the THM concentration does increase over the four day holding period. An excess ammonia seems to be needed to maintain the combined chlorine.

The finished water (using ammonia) was tested for taste and odors and thought to be of better quality than before. The plant superintendent granted permission to run the plant full-time based on the improvement in taste and odor, the excellent bacterial results, the decrease in THM concentration, and the minor increase in cost.

TABLE 11. COMPARISON OF TWO DIFFERENT RATIOS OF CHLORINE TO AMMONIA-NITROGEN

Parameter	2.9 Cl_2: 1 NH_3-N	4.5 Cl_2: 1 NH_3-N
Chlorine Residual, mg/l		
Free	.1 - .2	.1 - .2
Total	4.4	3.6
Ammonia-nitrogen, mg/l N	.7	.1
Inst. THM (ppb)		
$CHCl_3$	32	30
$CHCl_2Br$	4	4
4 day THM (ppb)		
$CHCl_3$	36	57
$CHCl_2Br$	5	6

Full-Scale Operation with Combined Chlorine

Based on the preliminary work previously discussed, chloramines were introduced as the final disinfectant dose on a continuous full-scale basis beginning on May 10, 1978. The initial goal of this phase was to continuously run the plant in this mode for about 15 to 20 days. After this time, it was expected that the plant operation would revert back to free chlorination while the results were being analyzed. However, the addition of the ammonium sulfate resulted in a dramatic increase in the drinking water quality (taste, odor, and THM concentrations); and the municipal officials decided to continue the process without interruption, if possible. Consequently, the ammonium sulfate feed rate was decreased toward the end of May in order to keep the process continuous until additional ammonium sulfate could be received at the plant. This decrease in feed rate caused an increase in the THM concentrations in the distribution system, although the THM values were still substantially less than before the ammonium sulfate was used.

It was very critical during the first few days of full-scale operation to assure that adequate disinfection was occurring. Fifteen samples for total coliform testing were taken the first two days, and all test results

were negative for coliforms. Samples for total coliform testing were obtained every three days from within the distribution system. All results met standards except for two samples at the Country Kitchen.

The two samples at the Country Kitchen had 2 and 6 total coliforms/100 ml. These samples were thought to have been contaminated while sampling. The faucet where the samples were taken was located outside the building and near some refuse containers. It was a good possibility that air-borne bacteria may have entered the sterile bag while sampling. Sampling techniques were changed to minimize contamination and all samples thereafter were negative for total coliforms.

The first few days involved adjusting the ammoniator to an efficient but economical chlorine to ammonia-nitrogen ratio. Ranges of 4.5, 4.0, 3.5, and 3.0 parts of chlorine to one part ammonia-nitrogen by weight were chosen. These ranges are recommended by White (10) to be economical and yet adequate to form monochloramines without forming the dichloramines which cause taste and odor.

The four ranges of 4.5, 4.0, 3.5, and 3.0 were tested with samples for unionized ammonia collected at the effluent of the clear well (station 7). Results showed 1.3, 1.6, 2.1, and 2.9 mg/l of unionized ammonia-nitrogen, respectively. This indicated an adequate amount of ammonium sulfate was being added. Ammonia residuals varied slightly from day to day depending on the amount of ammonia in the raw water and plant operating conditions.

The major objective of this research was to use chloramines to reduce the THM concentrations in the plant effluent and at the consumer's tap. The five distribution system stations along with station 6 (above the gravity filters) and station 7 (clear well) were tested for THM on a bi-weekly basis between August 7, 1977 and until the introduction of chloramines on May 10, 1978. These THM results depict the type of water the consumer was obtaining with chlorine as the disinfectant. After chloramines were used as the secondary disinfectant, these same stations were sampled about every three days until June 3, 1978 to show the reduction in THM concentrations.

Concentrations for chloroform and bromodichloromethane during this period are given in Table 12. An obvious reduction is noted after the change over to combined chlorine on May 10, 1978. Trihalomethane values within the distribution system were generally less than 20 ppb of chloroform and 7 ppb of bromodichloromethane. The rise in concentrations for the samples of May 27 and June 3 reflect the decrease in ammonium sulfate being added to the system while additional chemical was awaited. The feed rate was adjusted to 5.5:1 which is greater than the recommended range of from 3-4 mg/l chlorine to 1 mg/l ammonia. Excess ammonia was not available to keep all of the chlorine in the combined form, resulting in free chlorine which promoted THM formation.

A plot of total THM values (numerical addition of $CHCl_3$ and $CHCl_2Br$ concentrations) is shown in Figure 18. Samples collected at the Masonic

TABLE 12. THM CONCENTRATIONS DURING TRANSITION PERIOD

Sampling Station	Sampling Date											
	April		May			May				May		June
	4	18	10	11	12	13	15	18	22	24	27	3
Clear Well (Sta. 7)												
$CHCL_3$, ppb	55	105	17	12	18			11	5	39		44
$CHCl_2Br$, ppb	4	9	8	5	7			6	3	5		4
Masonic Bldg.												
$CHCl_3$, ppb	113	124		223	62	18		16	7	15		60
$CHCl_2Br$, ppb	3	12		50	8	6		5	4	7		4
Ninth St. Standard												
$CHCl_3$, ppb	128	121		153	87		20	15	8	19	71	37
$CHCl_2Br$, ppb	4	14		29	15		7	3	4	6	5	2
Country Kitchen												
$CHCl_3$, ppb	134	139	165	62			16	18	7	17	71	47
$CHCl_2Br$, ppb	5	10	21	6			6	6	3	4	5	4
Drive-In Liquor												
$CHCl_3$, ppb	108	159	172	78	78		19	25	15	20	67	44
$CHCl_2Br$, ppb	14	21	19	20	10		7	9	3	12	5	4
Airport												
$CHCl_3$, ppb	298	156	210		121		168	26	12	11	69	66
$CHCl_2Br$, ppb	13	17	27		24		15	12	5	4	3	9

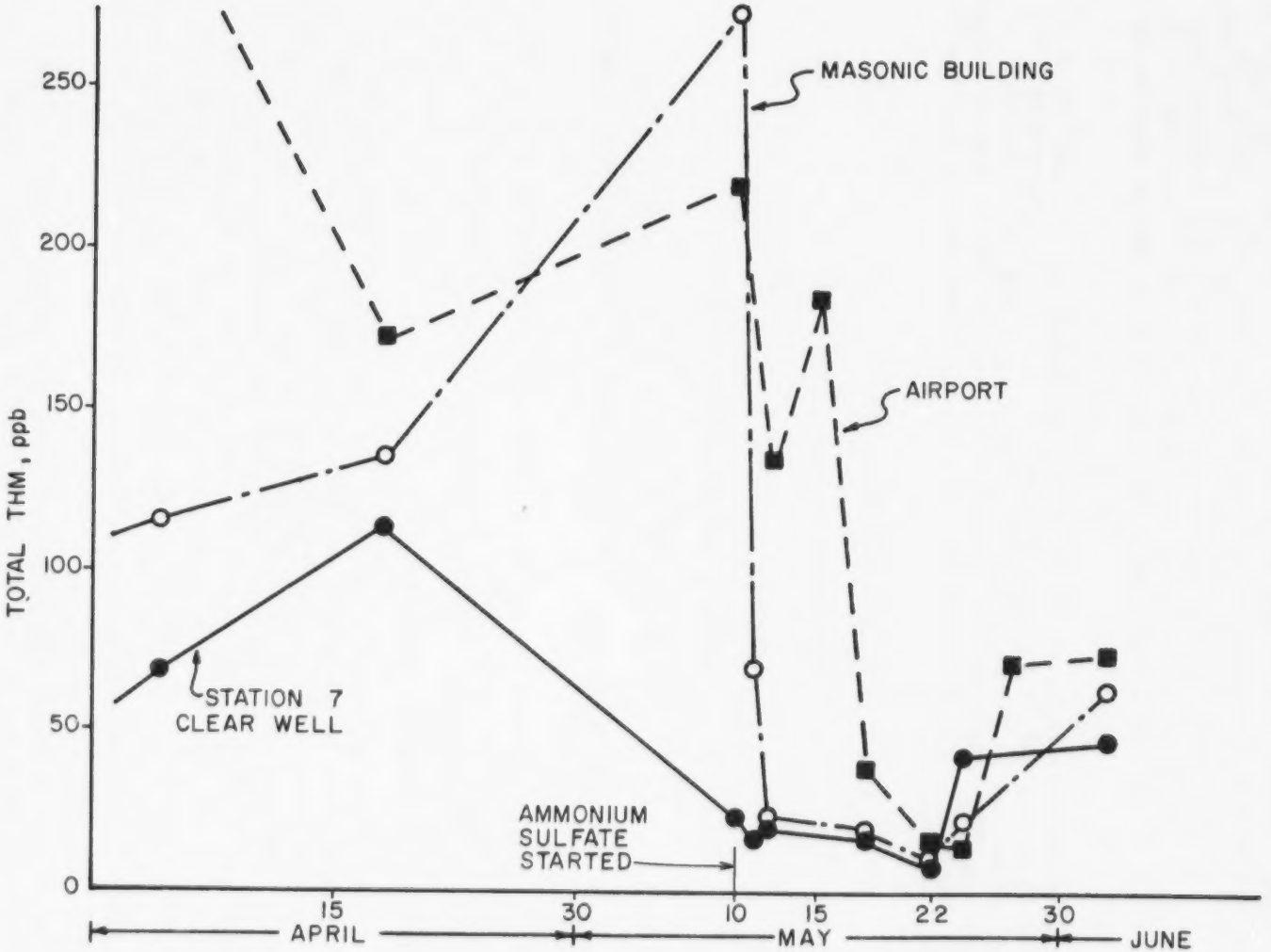

Figure 18. THM reduction using ammonium sulfate.

Building reflect the growth that occurs during a medium residence time in the distribution system. Those samples collected at the airport would be indicative of the growth that occurs during a long residence time. Again, the effect of the ammonium sulfate addition is clearly seen. It would seem that a total THM concentration at the tap of less than 50 ppb, and probably less than 25 ppb, should be easily obtainable with this method. The rise in concentrations at the end of May, again, is a result of a lowered ammonium sulfate feed rate.

The reductions in total THM by using chloramines was 37% and 50% at station 6 (above the filters)and station 7 (clear well), repectively. The average reduction in the distribution system, neglecting the transition period, was 75%. The total THM concentration dropped from an average value of 154 ppb to 37 ppb. The individual reductions at the various distribution sampling stations are:

Masonic Building--76%

9th Street Standard--75%

Country Kitchen--75%

Drive-in Liquor--72%

Airport--79%

It is believed Huron can maintain the total THM concentration below 30 ppb if:

(1) The pH is kept low at the point of application of chlorine, and

(2) A ratio of 3-4:1 chlorine:ammonia-nitrogen is applied.

Operation with Combined Chlorine

A noticeable decrease in the taste and odor of the finished water was evident to engineers, operators, and the public when the transition was made to combined chlorine. The raw water at Huron has a high organic content, sometimes exceeding 20 mg/l of total organic carbon. The finished drinking water was frequently the source of taste and odor complaints from consumers. In fact, the taste and odor of the finished water may be an adequate indicator of treatment for the water treatment plant operator. If the chlorine to ammonium sulfate ratio becomes too high, dichloramines are formed which result in an off taste to the water. At this point the operator knows that he needs to check the chemical feed rates and possibly increase the ammonium sulfate feed rate.

The above statement was verified during the summer of 1978. A spot check of the operation on June 27, 1978 yielded the information displayed in Table 13. At this time, some taste and odor problems were evident. The ammonium sulfate feeder was adjusted with a subsequent decrease in THM

concentrations. On July 14 the plant was producing 53 ppb of chloroform and 8 ppb of bromodichloromethane in the finished water (station 7). An increase of about 15 ppb was obtained for chloroform within the distribution system, while a change in the bromodichloromethane concentration was not detected.

TABLE 13. THM CONCENTRATIONS ON JUNE 27, 1978

Station	$CHCl_3$, ppb	$CHCl_2Br$, ppb
Clear Well	65	11
Masonic Building	121	19
Country Kitchen	140	--

At this writing (February 1979) combined chlorine is still providing satisfactory results. The chlorine residual level is about 3 mg/l at the tap with only a trace amount (<0.2 mg/l) possibly present as free chlorine.

The only ill affect noticed to date of using ammonium sulfate was the excess ammonia residual in the tap water. This ammonia residual is not detrimental to human health but is harmful to aquatic life (17). Unionized ammonia (NH_3) should not exceed 0.02 ppm of ammonia-nitrogen for fish survival (18). The amount of ammonia in water varies with the pH and temperature. Table 14 shows the concentrations of ammonia ($NH_3+NH_4^+$) which contain an unionized ammonia concentration of 0.02 ppm of ammonia-nitrogen.

TABLE 14. AMMONIA CONCENTRATIONS WHICH RESULT IN 0.2 mg/l UNIONIZED AMMONIA (NH_3)

Temperature °C	pH 6.0	7.0	8.0	9.0	10.0
20	51.9	5.20	.539	.072	.025
25	36.3	3.65	.384	.056	.024
30	25.6	2.58	.276	.046	.023

The excess ammonia in Huron's tap water resulted in some fish kills in aquariums throughout the city. Aquarium temperatures range from 21° - 27°C (23°C optimum) and Huron's pH at the tap ranges from 8.4-9.6. The maximum contaminant levels of ammonia for these ranges are 0.03 to 0.21 ppm ammonia-nitrogen (18). Since these low ammonia levels would be almost impossible to

maintain by the plant operators, other solutions were necessary. The excess ammonia is necessary to reduce THM formation and cannot be controlled and reduced adequately to meet the maximum contaminant level for fish.

The most realistic solution is to adjust the pH to 7. This allows an ample margin of safety (See Table 9-9) for fish survival. A pH of 7 is also the optimum pH for tropical fish survival, growth, and reproduction. Chemicals for pH adjustment are normally available at retail outlets which market tropical fish.

Total plate counts are sometimes used as a check on the bacterial quality of a finished drinking water. There is no sanitary significance in testing for total plate counts. A low total plate count does not indicate a disinfected water and on the other hand a high total plate count does not signify a contaminated water. High bacterial counts will sometimes interfere with the membrane filter technique for testing coliforms.

Total plate counts were performed before and after changing the disinfection procedure. Three sets of samples were taken when chlorine was being used and one set when chloramines were used. The results (Table 15) show chloramines did not deteriorate the disinfection capabilities of the water but actually enhance disinfection. Of course, one would expect a high bacterial count in October and November and samples with a lesser count during the spring (April and May). However, a 52% decrease in total plate counts was obtained from April to May by switching to combined chlorine.

TABLE 15. EFFECT OF CHLORINE VS CHLORAMINES ON TOTAL PLATE COUNTS

	Total Plate Count/ml; Type of Disinfection			
Station	10/30/77 Chlorine	11/ 6/77 Chlorine	4/ 5/78 Chlorine	5/15/78 Chloramines
#7 (Clear Well)	188	880	111	12
Masonic Bldg.	188	980	139	39
9th Street Standard	149	620	133	119
Drive-in Liquor	1000	5210	126	67
Country Kitchen	219	620	83	111
Airport	6380	6140	121	23

Economics

The addition of ammonia will increase the price of water treatment. The amount of ammonia added for treatment is dependent upon the chlorine dose. The maximum chlorine dose added in 1977-1978 was 840 pounds of chlorine per

day. At a 3:1 chlorine:ammonia-nitrogen ration by weight, the maximum cost of ammoniating (using ammonium sulfate) would be about 4¢/1000 gallons at current prices. The average chemical cost of chloramination was about 2¢/1,000 gallons at Huron during 1978. Currently high-grade ammonium sulfate, suitable for drinking water, can be obtained for $0.175 per pound.

One important comparison of chloramines with ozone, chlorine dioxide, and GAC is cost. Table 16 shows an estimate of the costs for various disinfection alternatives based on a 5 MGD plant. J. M. Symons et al. (14) compiled these costs and they are based on installing and operating new facilities with no existing equipment.

TABLE 16. ESTIMATED COSTS OF DISINFECTION ALTERNATIVES FOR A 5 MGD PLANT

Alternative	Cost in ¢/1000 gallons		
	Operating	Capital	Total
Chlorine (2ppm)	0.56	0.88	1.44
Ozone (1ppm)	1.05	1.36	2.41
Chlorine dioxide (1ppm)	1.18	0.76	1.90
Chloramines (3ppm)	0.78	0.89	1.67

These data reveal chloramines to be an economical solution to reduce THM formation. It should be remembered that most plants already have existing facilities for chlorination and only equipment to add ammonia would be necessary.

REFERENCES

1. Symons, J. M. et al. National Organics Reconnaissance Survey for Halogenated Organics. Jour. AWWA, 67:11:634 (Nov. 1975).

2. Harms, L. L. & Looyenga, R. W. Formation and Removal of Halogenated Hydrocarbons in Drinking Water. EPA 908/3-77-001, U.S. Environmental Protection Agency, Denver, Colo. (Jan. 1977).

3. Summary Report Water Quality and Return Flow Study, Initial Stage - Oahe Unit. Missouri-Oahe Projects Office, Huron, S.D. (Sept. 1975).

4. J. T. Banner and Assoc., Inc. "Report on Water Supply System and Proposed Improvements for City of Huron, S. Dak." Brookings, S.D. (May 1975).

5. Standard Methods for the Examination of Water and Wastewater. APHA, AWWA, WPCF, Washington, D.C. (14th ed., 1975).

6. Bellar, T. A. and Lichtenberg, J. J. Determining Volatile Organics at Microgram Per Litre Levels by Gas Chromatography. Jour. AWWA, 66:12:739 (Dec. 1974).

7. Stevens, A. A. & Symons, J. M. Measurement of Trihalomethane and Precursor Concentration Changes. Jour. AWWA, 69:10:546 (Oct. 1977).

8. Interim Primary Drinking Water Regulations, Control of Organic Chemical Contaminants in Drinking Water. U.S. Environmental Protection Agency, Federal Register, Feb. 9, 1978, Part II.

9. Race, J. Chlorination and Chloramines. Jour. AWWA, 5:3:79 (Mar. 1918).

10. White, G. C. Handbook of Chlorination. Van Nostrand Reinhold Co., New York, N.Y. (1972)

11. Butterfield, C. T. Bactericidal Properties of Free and Combined Available Chlorine. Jour. AWWA, 40:12:1305 (Dec. 1948).

12. Babbitt, H. E. et al. Water Supply Engineering. 6th Ed., McGraw Hill Book Co. New York, N.Y. (1962).

13. Willey, B. F. et al. Chicago's Switch to Free Chlorine Residual. Jour. AWWA, 67:8:438 (Aug. 1975).

REFERENCES (continued)

14. Symons, J. M. et al. Ozone, Chlorine Dioxide, and Chloramines as Alternatives to Chlorine for Disinfection of Drinking Water, State-of-the-Art. U.S. Environmental Protection Agency, Cincinnati, Ohio (Nov. 1977).

15. Cookson, J. T., and Arguero, R. C. Chlorinated Organics Evolving from Disinfection Practices - A Review of State of the Art Research.

16. Pelczar, M. J., and Reid, R. D., Microbiology, 3rd ed., McGraw-Hill Book Co., New York, N.Y. (1972).

17. McKee, J. E., and Wolf, H. W. "Water Quality Criteria." Publication 3-A, Calif. State Water Quality Control Board, Sacramento, CA (1963).

18. Willingham, W. T. Ammonia Toxicity. EPA 908/3-76-1, U.S. Environmental Protection Agency, Denver, CO (Feb. 1976).

APPENDIX A

FULL PLANT AND DISTRIBUTION SYSTEM DATA

TABLE A1. CHLOROFORM AND BROMODICHLOROMETHANE CONCENTRATIONS IN RAW WATER

Date	$CHCl_3$ (ppb)	$CHCl_2Br$ (ppb)
7/ 7/77	ND	ND
7/ 8/77	ND	ND
7/13/77	ND	ND
8/ 3/77	ND	ND
8/ 6/77	ND	ND
8/18/77	ND	ND
10/29/77	ND	ND
11/15/77	ND	ND
11/29/77	ND	ND
1/ 4/78	ND	ND
1/18/78	ND	ND
1/30/78	ND	ND
2/13/78	ND	ND

ND = Not Detectable

TABLE A2. CHLOROFORM AND BROMODICHLOROMETHANE CONCENTRATIONS FOR STATION NO. 3

Date	$CHCl_3$ (ppb)	$CHCl_2Br$ (ppb)
7/ 7/77	ND	ND
7/ 8/77	ND	ND
7/13/77	ND	ND
8/ 3/77	ND	ND
8/ 6/77	153	< 5
8/18/77	21	ND
10/29/77	81	< 1
11/15/77	62	< 1
11/29/77	78	6

ND = Not Detectable

TABLE A3. DATA ABOVE GRAVITY FILTERS (STATION 6).

Date	pH	Chlorine (ppm) Free	Chlorine (ppm) Total	$CHCl_3$ (ppb)	$CHCl_2Br$ (ppb)	Tot. Coliform 100 ml
7/ 7/77				29	18	
7/ 8/77				44	ND	
7/13/77				33	31	
8/ 3/77	10.2			50	5	
8/ 5/77*	9.3			94	5	
10/29/77*	9.5			81	1	
11/15/77*	9.3			62	4	
11/29/77*	9.2			78	5	
NEW WATER PLANT START-UP						
1/ 4/78	8.9			32	12	
1/18/78	9.5			11	7	
1/30/78	9.6			5	3	
2/13/78	9.5			4	2	
3/ 3/78	9.6			4	3	
3/13/78	9.3			6	9	
3/24/78	9.3			11	7	
4/ 4/78*	7			43	2	
4/18/78*	8.9			40	4	
STARTED AMMONIUM SULFATE						
5/10/78	8.6	0.05	0.6	30	9	
5/18/78				3	1	
5/22/78	9.1	0.3	0.4	3	1	
5/24/78	9.2	0.2	1.7	11	1	15
5/26/78	9.2	0.2	1.6			6
5/27/78	9.4	0.3	1.9	62	1	21
5/31/78	9.0	0.1	1.5			
6/ 3/78	8.3	0.7	1.6	29	3	

NOTE: All samples dechlorinated upon sampling
* Pre-chlorinating at high pH.

ND = Not Detectable

TABLE A4. DATA AT EFFLUENT OF CLEAR WELL (STATION 7)

Date	pH	Chlorine (ppm) Free	Chlorine (ppm) Total	$CHCl_3$ (ppb)	$CHCl_2Br$ (ppb)	Tot. Coliform 100 ml
7/ 7/77				36	ND	
7/ 8/77				48	20	
7/13/77				38	20	
8/ 3/77	9.3			62	5	
8/ 5/77*	8.9			63	5	
10/29/77*	8.0			86	6	
11/15/77*	8.1			66	3	
11/29/77*	9.0			42	4	
NEW WATER PLANT START-UP						
1/ 4/78	8.9			49	22	
1/18/78	9.4			54	12	
1/30/78	9.0	2.7	3.0	34	11	
2/13/78	8.4	>3.0	>3.0	23	6	
2/27/78	8.7	>3.0	>3.0	17	8	
3/13/78	8.2	>3.0	>3.0	27	17	
3/24/78	7.4	6.4	9.2	26	6	
4/ 4/78*	9.5	6.0	10.0	55	4	
4/18/78*	8.4	2.1	2.4	105	9	
STARTED AMMONIUM SULFATE						
5/10/78	8.7	2.8	4.0	17	7	0
5/10/78	---	0.1	3.7	17	9	0
5/11/78	8.6	0.15		12	5	0
5/12/78	8.2	0.3	6.8	18	7	0
5/12/78	7.8	0.2	5.2	12	3	
5/18/78	---			11	6	
5/22/78	8.7	0.1	2.7	5	3	
5/24/78	8.6	0.3	2.6	39	5	0
5/27/78	9.4	0.4	3.6			0
5/31/78	8.5	0.3	2.5			0
6/ 3/78	8.6	0.2	2.1	44	4	

NOTE: All samples dechlorinated upon sampling
*Pre-chlorinating at high pH.

ND = Not Detectable

TABLE A5. DATA AT MASONIC BUILDING

Date	pH	Chlorine (ppm) Free	Chlorine (ppm) Total	Tot. Coliform 100 ml	$CHCl_3$ (ppb)	$CHCl_2Br$ (ppb)
7/ 7/77					89	28
7/13/77					102	53
8/ 3/78	9.1				117	88
8/ 5/78	8.7				260	152
8/18/78					119	18
10/29/78*	8.3				116	48
11/15/78*	8.8				134	47
11/29/78*	8.7				92	14
NEW WATER PLANT START-UP						
1/ 4/78	9.3				98	19
1/18/78	9.1	1.3	2.0		111	26
1/30/78	9.2	2.1	3.0		81	44
2/13/78	8.7	0.5	1.5		66	52
3/ 3/78	8.2	0.63	1.6		84	47
3/13/78	8.3	0.4	1.1		66	51
3/24/78	7.2	2.9	4.6		83	18
4/ 4/78*	8.1	2.4	4.4		113	3
4/18/78*	8.9	1.9	2.4		124	12
STARTED AMMONIUM SULFATE						
5/11/78		0.3	1.7	0	223	50
5/12/78		0.3	2.3	0	62	8
5/13/78		0.18	3.2		18	6
5/18/78					16	5
5/22/78		0.4	2.4		7	4
5/24/78	8.5			0	15	7
5/26/78	8.8	0.2	2.2	0		
5/27/78	9.3	0.3	2.3	0		
5/31/78	9.0	0.3	2.7			
6/ 3/78	9.2	0.3	2.7		60	4

NOTE: All samples dechlorinated upon sampling
*Pre-chlorinating at high pH.

TABLE A6. DATA AT 9TH STREET STANDARD/A&M RADIO

Date	pH	Chlorine (ppm) Free	Chlorine (ppm) Total	Tot. Coliform 100 ml	$CHCl_3$ (ppb)	$CHCl_2Br$ (ppb)
8/18/77					80	28
10/29/77*	8.6				42	56
11/15/77*	9.0				134	40
11/29/77*	8.7				100	38
STARTED NEW WATER PLANT						
1/ 4/78					113	21
1/18/78	9.1	1.2	1.9		92	19
1/30/78	9.2	2.2	2.7		80	34
2/13/78	8.7	1.0	1.8		89	55
3/ 3/78	8.2	0.7	1.5		98	51
3/13/78	8.7	0.4	1.0		71	38
3/24/78	7.6	0.3	1.3		72	14
4/ 4/78*	7.7	2.6	3.0		128	4
4/18/78*	9.1	1.8	2.2		121	14
STARTED USING AMMONIUM SULFATE						
5/11/78		0.1	1.0	0	153	29
5/12/78	8.7	0.15	1.8	0	87	15
5/15/78	9.1	0.13	3.1		20	7
5/18/78					15	3
5/22/78	8.8	0.5	2.6		8	4
5/24/78	8.4	0.3	1.9	0	19	6
5/26/78	8.8	0.3	2.1	0		
5/27/78	9.3	0.4	2.4	0	71	5
5/31/78	9.2	0.2	2.3			
6/ 3/78	9.3	0.3	2.6		37	2

NOTE: All samples dechlorinated upon sampling
*Pre-chlorinating at high pH.

TABLE A7. DATA AT COUNTRY KITCHEN

Date	pH	Chlorine (ppm) Free	Chlorine (ppm) Total	Tot. Coliforms 100 ml	$CHCl_3$ (ppb)	$CHCl_2Br$ (ppb)
10/29/77*	8.4				111	40
11/15/77*	9.0				179	56
11/29/77*	9.0				102	17
STARTED NEW WATER PLANT						
1/ 4/77	9.4				124	50
1/18/78	9.1	1.2	2.0		116	31
1/30/78	9.1	2.1	2.7		95	31
2/13/78	8.6	.9	1.3		78	46
3/ 3/78	8.1	.9	1.2		89	59
3/13/78	8.6	.6	.9		65	55
3/24/78	7.6	.6	1.0		88	12
4/ 4/78*	7.9	2.2	2.8		134	5
4/18/78*	8.6	1.4	1.8		139	10
STARTED USING AMMONIUM SULFATE						
5/10/78	8.9	0.98	1.5		165	21
5/11/78		1.0	1.5	0	62	6
5/12/78	8.7	0.15	2.3	6		
5/15/78	9.1	0.1	3.1		16	6
5/18/78					18	6
5/22/78	8.8	0.4	2.4		7	3
5/24/78	8.8	0.3	1.8	2	17	4
5/26/78	8.7	0.4	2.0	0		
5/27/78	9.3	0.3	2.5	0	71	5
5/31/78	9.6	0.3	2.2			
6/ 3/78	9.6	0.4	2.5		47	4

NOTE: All samples dechlorinated upon sampling
*Pre-chlorinating at high pH.

TABLE A8. DATA AT DRIVE-IN LIQUOR

Date	pH	Chlorine (ppm) Free	Chlorine (ppm) Total	Tot. Coliform 100 ml	$CHCl_3$ (ppb)	$CHCl_2Br$ (ppb)
8/18/77					117	62
10/29/77*	8.2				97	33
11/15/77*	8.9				143	59
11/29/77*	8.7				103	4
STARTED NEW WATER PLANT						
1/ 4/78	9.3				101	13
1/18/78	8.1	0.1	1.9		107	29
1/30/78	9.2	1.6	2.5		92	39
2/13/78	8.7	0.2	1.2		84	59
3/ 3/78	8.2	0.4	1.2		88	61
3/13/78	8.4	0.2	0.9		67	41
3/24/78	8.8	0.4	1.7		85	12
4/ 4/78*	8.0	2.7	4.4		108	14
4/18/78*	8.8	1.5	1.8		159	21
STARTED USING AMMONIUM SULFATE						
5/10/78	9.0	0.8	1.2		172	19
5/11/78	8.9	0.3	1.2	0	78	20
5/12/78	8.7	0.15	2.3	0	78	10
5/15/78	9.0	0.2	3.2		19	7
5/18/78					25	9
5/22/78	8.8	0.5	2.4		15	3
5/24/78	8.8	0.2	2.3	0	20	12
5/26/78	8.7	0.2	2.2	0		
5/27/78	9.4	0.4	2.7	0	67	5
5/31/78	9.0	0.2	2.3			
6/ 3/78	9.0	0.2	2.1		44	4

NOTE: All samples dechlorinated upon sampling
*Pre-chlorinating at high pH.

TABLE A9. DATA AT THE AIRPORT

Date	pH	Chlorine (ppm) Free	Chlorine (ppm) Total	Tot. Coliform 100 ml	$CHCl_3$ (ppb)	$CHCl_2Br$ (ppb)
7/ 7/77					134	49
7/13/77					84	ND
8/ 3/77	9.7				196	103
8/ 5/77					279	163
8/18/77					113	28
10/29/77*	9.4				154	60
11/15/77*	9.4				150	42
11/29/77*	9.2				189	42
STARTED NEW WATER PLANT						
1/ 4/78	9.4				109	48
1/18/78	9.2	0.4	1.1		181	51
1/30/78	9.2	0	0.7		107	68
2/13/78	9.0	0	0.8		107	63
3/ 3/78	8.3	0.2	1.0		148	88
3/13/78	9.0	0.1	1.4		69	59
3/24/78	7.1	0.1	2.1		79	20
4/ 4/78*	9.0	2.3	3.0		298	13
4/18/78*	9.0	0.8	1.2		156	17
STARTED USING AMMONIUM SULFATE						
5/10/78	9.1	0.4	0.95		210	27
5/12/78	9.3	0.85	1.35	0	121	24
5/15/78	9.4	0.1	3.1		168	15
5/18/78					26	12
5/22/78	9.3	0.3	2.6		12	5
5/24/78	9.5	0.2	2.4	0	11	4
5/26/78	8.6	0.2	2.3	0		
5/27/78	9.4	0.3	2.2	0	69	3
5/31/78	9.3	0.2	2.2			
6/ 3/78	9.4	0.2	2.3		66	9

NOTE: All samples dechlorinated upon sampling
*Pre-chlorinating at high pH.
ND = Not Detectable

APPENDIX B

RESIDENCE TIME IN THE DISTRIBUTION SYSTEM

TABLE B1. RESIDENCE TIMES IN THE DISTRIBUTION SYSTEM, CHLORAMINES STUDY

Station	Starting Chlorine Residual (ppm)		Final Chlorine Residual (ppm)		Time from Chloramines Introduction
	Free Cl_2	Total Cl_2	Free Cl_2	Total Cl_2	
Masonic Building	1.2	2.2	0.3	1.7	15 hours
A&M Radio	1.2	2.2	0.1	1.0	15 hours
Drive-in Liquors	0.8	1.2	0.3	1.2	15-18 hours
Country Kitchen	1.0	1.5	0.3	1.8	15-26 hours
Airport	0.4	0.9	0.1	3.1	4.75 days

APPENDIX C

PIPE MATERIAL TEST

TABLE C1. PIPE MATERIAL TEST NO. 1

Parameters

Chlorine Demand Free Water
Chlorine Dose (free) 3.43 ppm
pH=11
Time=24 hours
Temperature=20°C

Pipe Material Added (g/l)	Chlorine Residual		PTHM	
	Free (ppm)	Total (ppm)	$CHCl_3$ (ppb)	$CHCl_2Br$ (ppb)
0.0	2.68	3.18	5	2
0.0	3.45	3.6	5	4
0.1	2.80	2.80	11	5
0.1	3.00	3.00	14	4
0.5	1.35	1.35	19	ND
0.5	1.35	1.5	37	ND
1.0	0.89	0.91	33	4
1.0	0.81	1.00	30	5
5.0	0.03	0.18	19	4
5.0	0.03	0.09	18	6

ND=Not Detectable

TABLE C2. PIPE MATERIAL TEST NO. 2

Parameters

Chlorine Demand Free Water
Chlorine Dose (free) 18.20 ppm
pH=11
Time=24 hours
Temperature=20°C

Pipe Material Added (g/l)	Chlorine Residual		PTHM	
	Free (ppm)	Total (ppm)	$CHCl_3$ (ppb)	$CHCl_2Br$ (ppb)
0.0	0.68	7.8	19	ND
0.0	0.60	8.6	17	ND
5.0	0.35	0.72	95	ND
5.0	1.05	1.38	109	ND
10.0	0.35	0.58	97	ND
10.0	0.08	0.35	83	ND
20.0	0.88	1.38	63	ND
20.0	0.05	1.08	62	ND

ND=Not Detectable

APPENDIX D

IN PIPE TEST

TABLE D1. IN PIPE TEST OF APRIL 4, 1978

Time (hours)	Pipe		Chlorine Residual	
	$CHCl_3$ (ppb)	$CHCl_2Br$ (ppb)	Free Cl_2 (ppm)	Total Cl_2 (ppm)
0	108	8	1.8	2.4
1	133	8	1.8	2.4
2	130	3	1.2	2.4
4	159	7	1.4	1.9
12	152	6	1.4	2.3
24	155	6	1.2	1.7
48	174	10	0.1	0.4

TABLE D2. IN PIPE TEST OF APRIL 4, 1978

Time (hours)	Baseline		Chlorine Residual	
	$CHCl_3$ (ppb)	$CHCl_2Br$ (ppb)	Free Cl_2 (ppm)	Total Cl_2 (ppm)
0	108	2	1.8	2.4
1	138	7	-	-
2	137	7	-	-
4	145	10	-	-
12	155	7	-	-
24	160	8	-	-
48	196	14	1.1	1.5
72	196	6	1.3	1.5
96	-	-	-	-
120	199	8	0.8	1.0
144	203	7	0.8	1.0

TABLE D3. IN PIPE TEST OF MAY 7, 1978

Time (hours)	Pipe		Chlorine Residual	
	$CHCl_3$ (ppb)	$CHCl_2Br$ (ppb)	Free Cl_2 (ppm)	Total Cl_2 (ppm)
0	198	42	1.2	1.5
12	194	32	0.6	1.0
24	188	50	0.4	0.8
48	219	50	0.0	0.5

TABLE D4. IN PIPE TEST OF MAY 7, 1978

Time (hours)	Baseline		Chlorine Residual	
	$CHCl_3$ (ppb)	$CHCl_2Br$ (ppb)	Free Cl_2 (ppm)	Total Cl_2 (ppm)
0	161	11	1.2	1.5
12	183	29	-	-
24	197	49	-	-
48	180	25	-	-
96	226	30	-	-
144	248	41	-	-
192	236	41	-	-
240	266	48	0.60	0.95

APPENDIX E

RAW WATER QUALITY DATA

TABLE E1. PHYSICAL WATER QUALITY DATA FOR THE RAW WATER

Date	Temp. (°C)	pH	Specific Conductance (umhos/cm) @ 25°C	Total Residue (ppm)	Chemical Oxygen Demand (ppm)	Turbidity (NTU)
7/ 7/77	-	8.0	940	675	66	28.0
7/ 8/77	-	8.4	940	675	56	22.0
7/13/77	-	8.5	1080	764	88	22.0
8/ 3/77	-	8.9	1053	805	190	30.0
8/ 5/77	-	8.9	1228	791	55	35.0
8/18/77	-	-	1131	770	22	31.0
9/21/77	-	8.3	1262	-	64	27.0
10/29/77	15.0	8.9	1366	457	34	-
11/15/77	6.0	8.8	1216	912	35	-
11/29/77	5.0	8.8	1315	-	38	6.0
1/ 4/78	4.0	8.5	1629	1130	23	6.0
1/18/78	3.0	9.1	1732	1260	15	5.0
1/30/78	3.0	7.8	2268	1691	54	4.0
2/13/78	4.0	7.8	2900	2209	54	2.0
2/27/78	4.0	7.2	2887	2520	60	12.0
3/10/78	3.0	7.7	1804	1257	-	8.0
3/13/78	3.0	7.7	1753	1158	26	7.0
3/24/78	3.0	7.6	464	339	44	18.0
4/ 4/78	7.0	7.5	4000	263	73	21.0
4/18/78	7.0	7.1	4600	312	36	31.1
5/ 2/78	13.5	8.8	496	329	24	7.4
5/10/78	10.0	8.6	590	405	29	6.7

TABLE E2. PHYSICAL WATER QUALITY DATA FOR THE RAW WATER

Date	Suspended Solids (ppm)	Volatile Suspended (ppm)	NH_3-N (ppm)	PTHM	
				$CHCl_3$ (ppb)	$CHCl_2Br$ (ppb)
7/ 7/77	127.0	42	-	-	-
7/ 8/77	59.0	29	-	-	-
7/13/77	34.0	20	0.06	-	-
8/ 3/77	84.0	56	0.13	-	-
8/ 5/77	47.0	12	0.10	-	-
8/18/77	42.0	14	0.03	-	-
9/21/77	52.2	-	-	-	-
10/29/77	29.0	17	0.04	-	-
11/15/77	14.0	-	1.03	-	-
11/29/77	10.0	5	0.13	-	-
1/ 4/78	12.0	7	0.16	-	-
1/18/78	7.7	1.1	-	371	45
1/30/78	15.0	7	0.81	-	-
2/13/78	5.0	1	0.05	-	-
2/27/78	10.0	7	0.41	408	56
3/10/78	9.0	7	0.27	340	58
3/13/78	13.0	7	0.37	300	7
3/24/78	44.0	17	-	250	ND
4/ 4/78	59	6	-	530	7
4/18/78	46	8	-	603	5
5/ 2/78	15	5	0.01	-	-
5/10/78	31	3	-	-	-

APPENDIX F

PTHM VS. CHLORINE DOSE

TABLE F1. PTHM VS. CHLORINE DOSE SEPTEMBER 21, 1977

Parameters

Temperature=20°C
Time=24 hours
pH=8.3
Raw Water Huron, South Dakota

Free Chlorine Dose (ppm)	Chlorine Residual		PTHM	
	Free (ppm)	Total (ppm)	$CHCl_3$ (ppb)	$CHCl_2Br$ (ppb)
5.2	0.27	0.82	22	ND
10.4	0.27	0.68	43	ND
20.8	0.48	1.57	93	26
41.6	28.12	35.62	164	22

TABLE F2. PTHM VS. CHLORINE DOSE MARCH 24, 1978

Parameters

Temperature=20°C
Time=96 hours
pH=11
Raw Water From Huron, South Dakota

Free Chlorine Dose (ppm)	Chlorine Residual Free (ppm)	Chlorine Residual Total (ppm)	PTHM $CHCl_3$ (ppb)	PTHM $CHCl_2Br$ (ppb)
9.9	0.75	0.88	51	27
19.8	0.05	0.15	131	6
29.7	0.05	0.30	523	39
39.6	0.09	0.55	586	45

TABLE F3. PTHM VS. CHLORINE DOSE MAY 10, 1978

Parameters

Temperature=20°C
Time 96 hours
pH=11
Raw Water From Huron, South Dakota

Free Chlorine Dose (ppm)	Chlorine Residual Free (ppm)	Chlorine Residual Total (ppm)	PTHM $CHCl_3$ (ppb)	PTHM $CHCl_2Br$ (ppb)
4.2	0.05	0.21	155	16
21.1	10.40	12.60	1959	112
31.60	22.00	23.00	1601	106
42.13	31.50	33.00	1882	111

APPENDIX G

CHLORINE DOSE AT THE TREATMENT PLANT

TABLE G1. PRECHLORINE PLUS POSTCHLORINE DOSE

Date	Chlorine Dose (ppm)
1/18/78	10.21
1/30/78	12.93
2/13/78	13.34
2/27/78	13.97
3/13/78	19.17
3/24/78	20.87
4/ 4/78	11.49
4/18/78	9.2
5/ 2/78	6.18
5/10/78	6.59

APPENDIX H

RIVER TRIP DATA

TABLE H1. WATER QUALITY DATA, RIVER TRIP JULY 13, 1977

River Miles	pH	Specific Conductance (umhos/cm @ 25°C)	Chemical Oxygen Demand (ppm)	Turbidity (NTU)
0.00	8.5	862	46	55
1.62	8.9	900	73	125
3.62	8.6	1202	81	85
7.41	8.4	1497	80	50
9.94	8.5	1449	65	35
11.37	8.7	1351	49	45
12.35	8.7	1322	107	52
13.69	9.0	1250	131	150
14.66	9.2	1137	147	135
15.56	8.8	991	168	152
15.75	8.8	1035	141	150
17.22	9.6	944	137	130
18.10	9.3	943	129	155
18.90	9.6	975	102	124
19.63	9.1	1008	54	70
20.12	9.0	994	-	62
21.37	9.1	966	72	60
22.34	9.0	1031	60.	40
23.34	9.2	961	76	50
24.31	9.1	1005	68	55
25.18	9.2	1065	60	53
26.47	9.0	1050	127	52
27.63	8.9	929	108	35
28.62	8.7	111	58	37

TABLE H2. WATER QUALITY DATA, RIVER TRIP JULY 13, 1977

River Miles	Suspended Solids (ppm)	Volatile Suspended Solids (ppm)	PTHM	
			$CHCl_3$ (ppb)	$CHCl_2Br$ (ppb)
0.00	100	22	1300	244
1.62	182	47	2350	358
3.62	188	56	2130	516
7.41	163	47	1620	597
9.94	142	49	1950	224
11.37	155	68	1790	459
12.35	315	21	1950	193
13.69	320	39	2500	429
14.66	251	48	3310	540
15.56	259	17	2230	105
15.75	222	117	2030	95
17.22	272	150	1400	50
18.10	275	126	2150	95
18.90	202	121	2540	185
19.63	128	93	1820	130
20.12	109	52	1630	115
21.37	107	59	1120	90
22.34	67	45	1100	50
23.34	108	56	764	50
24.31	101	45	1080	65
25.18	77	42	1540	170
26.47	81	37	706	50
27.63	54	20	1480	140
28.62	52	22	987	140

APPENDIX I

TOTAL ORGANIC CARBON DATA

TABLE II. TOTAL ORGANIC CARBON ANALYSES, HURON, SOUTH DAKOTA

Date	Station	Total Organic Carbon (ppm)
10/14/77	Raw Water	16.00
2/13/78	Raw Water	20.95
2/14/78	Raw Water	21.81
2/14/78	Clear Well	1.58
2/14/78	Airport	1.81
3/29/78	Raw Water	12.76
3/29/78	Primary Sedimentation	9.06
3/29/78	Upflow Basin	8.97
3/29/78	Above Filters	1.35
3/29/78	Below Filters	0.92
3/29/78	Clear Well	0.92

APPENDIX J

TOTAL COLIFORM DATA

TABLE J1. TOTAL COLIFORM COUNTS OVER A ONE AND A HALF HOUR PERIOD AT STATION 1 AND 5

Station	7/13/77 Time	Total Coliforms 100 ml
1	2:15 pm	5,800;10,500*
5	2:15 pm	10;27
1	2:45 pm	17,800;9,200
5	2:45 pm	25;27
1	3:15 pm	15,300;11,800
5	3:15 pm	65;55
1	3:45 pm	12,800;17,800
5	3:45 pm	15;50

*Duplicate Determinations

TABLE J2. TOTAL COLIFROM SAMPLES FROM STATION 2 AND THE EFFECT OF pH ON BACTERIAL SURVIVAL, JULY 20, 1977

Time (min.)	Total Coliforms/100 ml			
	pH 8	pH 9	pH 10	pH 11
0	13,500;11,900*			
15	12,400; 9,000	12,400;10,100	7,600; 7,000	2,600;2,000
30	12,800;10,900	6,200; 6,100	7,000; 6,600	2,200;1,400
60	18,200;12,900	9,800; 7,300	10,200:11,300	600; 680
120	31,600;19,500	16,400;13,800	3,400: 3,760	500; 600
140	17,400;12,500	22,800;19,400	13,300:12,120	0; 0

Note: Initial pH = 8.04, Temperature = 21°C

TABLE J3. TOTAL COLIFORM SURVIVAL AT STATION 2 USING MONOCHLORAMINE, JANUARY 25, 1978

NH_2Cl-Cl_2 Dose (ppm)	Total Coliforms/100 ml Detention Time (hrs.)	
	0.75	2.0
0	200;300	
2.5	0;0	0;0
5	0;0	0;0
10	0;0	0;0
15	0;0	0;0

*Duplicate Determinations

Note: pH = 7.8, Temperature = 4°C
4:1 Cl_2:NH_3-N (by weight)

TABLE J4. TOTAL COLIFORM SURVIVAL AT STATION 2 USING MONOCHLORAMINE AND pH, FEBRUARY 2, 1978

NH_2Cl-Cl_2 Dose (ppm)	Total Coliforms/100 ml Detention Time (hrs.) 0.5	1.75	3
0	1,250;972*		
2.5	0;0	0;0	0;0
5	0;0	0;0	0;0
10	0;0	0;0	0;0

*Duplicate Determinations

Note: pH = 10.5, Temperature = 3°C
4:1 Cl_2Cl_3NH -N (by weight)

TABLE J5. TOTAL COLIFORM SURVIVAL AT STATION 2 USING MONOCHLORAMINE, FEBRUARY 17, 1978

NH_2Cl-Cl_2 Dose (ppm)	Total Coliforms/100 ml Detention Time (hrs.) 0.5	2.0
0	15,000	
2.5	28	0
5	0	0
10	0	0

Note: pH = 7.8, 4:1 Cl_2NH_3-N (by weight)

APPENDIX K

ARTIFICIAL SPIKING DATA

TABLE K1. THM AND OTHER DATA IN DECHLORINATED SAMPLES DURING ARTIFICIAL SPIKING EXPERIMENT

Date	pH	Tot. Coliform 100 ml	$CHCl_3$ (ppb)	$CHCl_2Br$ (ppb)
3/ 3/78	9.5	0	4	3
3/10/78		0	4	2
3/15/78	9.6	0	5	3
3/17/78		0	5	3
3/25/78	8.8	0	8	7
3/28/78	9.1	0	8	10
4/ 4/78*	9.2	0	11	4
4/10/78*	9.6	0	10	4
4/18/78*	8.5	0	34	4
4/24/78*	10.5	0	40	4

*Pre-Chlorinated at high pH.

TABLE K2. THM AND OTHER DATA IN CHLORINATED SAMPLES DURING ARTIFICIAL SPIKING EXPERIMENT

Date	pH	Chlorine dose (ppm)	Chlorine Residual (ppm) Free	Total	$CHCl_3$ (ppb)	$CHCl_2Br$ (ppb)
3/ 3/78	9.5	9	0.1	1.6	47	21
3/10/78		9	0.1	2.6	38	14
3/15/78	9.6	9	0.1	1.71	42	14
3/17/78		15	0.0	0.2	40	18
3/25/78	8.8	20	0.9	1.65	79	27
3/28/78	9.1	20	9.4	10.4	36	22
4/ 4/78*	9.2	15	7.0	12.8	184	15
4/10/78*	9.6	15	6.7	7.1	149	12
4/18/78*	8.5	15	10.5	12	91	11
4/24/78*	10.5	15	10.4	11	101	9

*Pre-chlorinated at high pH.

TABLE K3. THM AND OTHER DATA IN AMMONIATED SAMPLES DURING ARTIFICIAL SPIKING EXPERIMENT

Date	pH	Tot. Coliform 100 ml	Chlorine Residual (ppm) Free	Total	Cl_2:NH_3-N Ratio	$CHCl_3$ (ppb)	$CHCl_2Br$ (ppb)
3/ 3/78	9.5	0	0.3	4.6	3:1	15	7
3/10/78		0	0.3	4.1	3:1	9	6
3/15/78	9.6	0	0.35	3.8	4:1	17	8
3/17/78		0	0.0	0.4	4:1	22	9
3/25/78	8.8	0	0.3	1.7	4:1	18	12
3/28/78	9.1	0	0.2	19.8	4:1	15	13
4/ 4/78*	9.2	0	0.15	12	4:1	117	6
4/10/78	9.6	0	0.2	13.4	4:1	64	6
4/18/78*	8.5	0	0.4	13.6	4:1	50	5
4/24/78*	10.5	0	0.4	3.1	2:1	45	5